# Spectroscopic Studies of Radiation Induced Defects in Natural and Synthetic Diamonds.

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# SPECTROSCOPIC STUDIES OF RADIATION INDUCED DEFECTS IN NATURAL AND SYNTHETIC DIAMONDS

by

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## Abstract

The subject matter of this thesis is composed of the results of spectroscopic investigations into the properties of several optical radiation damage systems in natural and synthetic type 1 diamond.

A survey has been made of radiation damage products in type 1b synthetic diamonds containing isolated nitrogen in concentrations of 10 p.p.m. to 200 p.p.m. in order to make a qualitative assessment of the nitrogen dependence of such radiation damage products. A previously undocumented cathodoluminescence system consisting of a doublet of emission lines of energy 794 meV and 797 meV has been observed, and has been qualitatively correlated with the well known 2.155 eV emission system which is produced by radiation damage of the intrinsic lattice. In addition, previously unreported absorption systems at 2.367 eV, 2.443 eV and 2.535 eV have been detected, as they have also been in a natural type 1b diamond.

The 2.367 eV system appears to be nitrogen dependent and has been observed to take part in a temperature dependent exchange of charge with other optical centres having zero phonon transitions below 2.367 eV. The 2.367 eV centres are apparently thermally repopulated with charge from the centres of lower energy, the activation energy for repopulation being $\sim$140 meV. The temperature dependence of the 2.367 eV zero phonon line has been analysed in terms of a Debye spectrum of phonons coupled to the centre involved and found to have a Huang-Rhys factor of 1.5 and a Debye phonon cut off energy of 65 meV.

The effects of controlled isothermal annealing of types 1a and 1b natural diamond have been studied over the range of temperatures 500-700$^{o}$C. A kinetic model of annealing has consistently shown that ND1 (nitrogen interstitial .) centres are responsible for production of the H3(503.2nm) and H4(496.5nm) absorption systems in type 1a diamond,

and the 640 nm absorption system in type 1b diamond. These systems are produced when the ND1 centres become mobile and are subsequently trapped at the various types of nitrogen impurity forms present in such diamonds.

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# Chapter 1.

# A review of the optical properties of diamond

## Sec. 1.1 Introduction

This chapter is a review of the optical properties of diamond. The optical phenomena associated with diamond have been no less a source of scientific interest than its exceptional hardness has been a source of wealth to the industrial world. The unusually high refractive index of about 2.4 in the visible spectral region was known to Newton, whilst Brewster commented upon its low dispersive power in 1813. Structure in the ultra-violet absorption spectra of diamonds was reported by Walter in 1891, whilst Crookes, in 1879, observed the emission of light from diamonds when bombarded by electrons. In 1905 Crookes diagnosed radiation damage as the cause of coloration of diamonds, a topic which will concern us throughout this work.

The pecuniary considerations which led to the desire for synthetic diamonds have provided us with a most useful means of studying the material because of the control which can be exercised over the nitrogen impurities present.

We shall now consider the present state of knowledge of optical phenomena in diamond.

## Sec. 1.2 Optical properties of the intrinsic diamond lattice.

Intrinsic diamond is found to have an indirect band gap, with a minimum in the conduction band at $k = \langle 0.76, 0, 0 \rangle$ , as determined from the shape of the fundamental absorption threshold

(Clark et al, 1964) in conjunction with the phonon dispersion curves obtained from slow neutron scattering by Warren et al (1967). The valence band exhibits a spin-orbit splitting of 7 meV (Dean and Jones, 1964) such splitting being manifested by the production of two components in the emission of radiation associated with band-gap recombinations. The fundamental absorption threshold was reported by Clark et al (1964) to occur at an energy of 5.480 eV at 100K.

Roberts and Walker (1967) have shown the direct energy gap of diamond to be about 7 eV, and, consequently, absorption caused by direct transitions is unobserved, as a result of the intense absorption produced by indirect transitions at this energy. The emission of radiation as a result of direct band gap transitions is unobserved since electrons which are excited deep into the conduction band rapidly lose energy and relax to the bottom of the conduction band from which indirect transitions are made.

In addition to absorption associated with electronic transitions between conduction and valence bands, diamond also exhibits optical absorption caused by excitation of vibrational modes of the lattice. The lack of a permanent electric dipole in the pure diamond lattice prohibits one phonon generation (Loudon, 1964); this has been verified experimentally by Smith et al (1960). The allowed two phonon absorption process has been observed by the latter authors, being seen in the region of about 0.18 eV to 0.33 eV. The one phonon absorption process has been detected, however, after radiation damage (Smith et al 1962), the results being consistent with those deduced from the two-phonon spectra. In addition, one-phonon absorption is induced in the lattice by the introduction of impurities. The effects of such introduction form the subject-matter

of sections 1.3 and 1.4.

## Sec. 1.3 The nitrogen impurity in diamond.

The first classification of diamond into two basic groups, as a result of discrepancies in the optical phenomena observed in different diamonds, was made by Robertson, Fox and Martin (1934, 1936). The so-called type II diamonds were found to exhibit those optical features typical of "pure" diamond, whilst type I diamond, in addition to such features, exhibited absorption at about 8$\mu$m (155 meV) in the infra-red region, and also in the ultra-violet region at energies rather lower than those associated with intrinsic band gap transitions. The infra-red absorption would appear to be due to impurity induced one-phonon excitation, and the strength of the absorption at 7.8$\mu$m has been shown by Kaiser and Bond (1959) to correlate with the nitrogen content of such diamonds. This correlation has been confirmed by Lightowlers and Dean (1964)who also showed that no other impurities were present in type I diamond in sufficient quantities to produce the observed absorption.

X-ray diffraction patterns of type I diamond have been found to exhibit anomalous intensity spikes (Lonsdale and Smith 1941), consistent with aggregates on ⟨100⟩ planes. These aggregates are known as platelets and have been shown by Evans and Phaal (1962) to be typically 60 nm to 100 nm in diameter, and, at most a few atoms thick. Elliott (1960) suggested that the platelets were, in fact, the cause of the infra-red absorption, being composed of nitrogen. Sobolev et al (1967) have shown, however, that no

correlation exists between absorption at 7.8$\mu$m and the concentration of such platelets. A correlation has been demonstrated by the same authors between platelet concentration and an absorption feature occurring in such diamonds at 7.3$\mu$m, the so-called B' feature.

It has been observed by Sutherland et al (1954) that the impurity induced one-phonon absorption spectrum could be subdivided into several groups of features. The components of each group correlated well with each other, but no correlation was found between the features of the different groups. The authors suggested that this could be attributed to a number of different impurity forms which produced absorption in this spectral region. The type of diamond now classified as type Ia seems to be characterized by the presence of at least two different forms of nitrogen aggregate in the lattice, the most prominent of which are called the A and B forms. Davies (1972) has demonstrated that the infra-red absorption spectra of type Ia diamond is amenable to decomposition in terms of the two basic, A and B, types of spectra, each having the same absorption, for a given nitrogen content, at 7.8$\mu$m. The two types of nitrogen aggregate might be expected to be of similar physical size and structure, an upper limit of 8 nitrogen atoms per aggregate having been estimated by Evans (1972). The 7.3$\mu$m B' feature associated with platelets in the lattice has no absorption associated with it at 7.8$\mu$m and it has been suggested by Davies (1970) that at most, 10% of the nitrogen in type Ia diamond is in platelet form, and it is conceivable that the platelet formation is completely independent of nitrogen.

In addition to vibrational spectra, nitrogen in type Ia

diamond has been found to give rise to an absorption continuum from about 3.75 eV to the fundamental absorption threshold (Clark et al, 1965).

A rare form of natural diamond (Dyer, Raal et al, 1965) is that in which nitrogen is present in the form of isolated substitutional atoms, producing the so-called type 1b diamond. All nitrogen doped synthetic diamonds are type 1b in form however (Charrette 1961, Huggins & Cannon 1962, Sobolev et al 1969, Chrenko et al 1971). The main feature associated with the presence of isolated nitrogen atoms is an electron paramagnetic resonance (e.p.r.) signal detected by Smith et al (1959). The latter authors observed that the e.p.r. spectrum of natural type 1b diamonds contained a triplet of equally spaced, equally intense components, which would arise from the presence of a nucleus of spin 1. The $N^{14}$ isotope was suggested as being the most likely of the few isotopes which have such a nuclear spin. The differences in the e.p.r. spectrum which occurred when the d.c. magnetic field was aligned along different crystallographic axes were found to be consistent with the nitrogen impurity atoms being located on substitutional sites

In addition, Smith et al observed that each of the nitrogen triplet lines of the e.p.r. spectrum showed two weak lines spaced symmetrically about the nitrogen resonances. This was interpreted as being due to the presence of small quantities of the $C^{13}$ isotope which comprises about 1% of natural carbon and has a nuclear spin of $\frac{1}{2}$.

Dyer et al (1965) observed similar e.p.r. spectra in synthetic type 1b diamond with the exception that the resonance lines were broader due to the presence of ferro-magnetic inclusions (Co, Ni, Fe) used in the growth of such diamonds.

Loubser and du Preez (1965) observed two weak e.p.r. lines equispaced from the central $N^{14}$ resonance line, which they interpreted as being due to the presence of the $N^{15}$ isotope of nitrogen, having spin $\frac{1}{2}$. The relative resonance positions of the $N^{15}$ and $N^{14}$ lines yielded the

ratio of the magnetic moments of these isotopes as being 0.72, in good agreement with the accepted value of 0.701.

Thus it is well established that nitrogen is present in type 1b diamond, occupying isolated substitutional sites whilst it is not present in this form in type 1a diamond in sufficient quantities to contribute to the observed optical absorption in that type of diamond (Smith et al 1959).

The presence of isolated nitrogen atoms gives rise to a characteristic one phonon absorption process which exhibits a peak at 8.85$\mu$m (140 meV). Also observed is a broad absorption continuum commencing at about 1.7eV and continuing to the fundamental absorption threshold. Superimposed on this continuum is an absorption peak at 270 nm (4.58 eV) (Chrenko et al, 1971). Both the 140 meV and 4.58 eV absorption peaks have been shown by Chrenko et al to correlate with the e.p.r. signal caused by the nitrogen impurity over a wide range of nitrogen concentrations in synthetic diamonds. Chrenko has derived the relationship that 25 p.p.m. nitrogen produces an absorption coefficient of 1 $cm^{-1}$ at 140 meV and of 45 $cm^{-1}$ at 4.85 eV. Whilst in qualitative agreement with Sobolev et al (1969), the above results show a concentration some three times higher than those deduced by Sobolev for a given value of either of the absorption

coefficients. The results of Chrenko were produced as a result of work on larger, more homogeneous diamonds than those of Sobolev, and would hence appear to be more reliable. The typical absorption produced by yellow (high nitrogen content) and colourless (low nitrogen content) synthetic diamonds, as observed by Chrenko, is shown in fig. 1.1.

In addition to absorption, type Ia and type Ib diamonds exhibit characteristic cathodoluminescence spectra. Type Ia diamonds show a broad emission band from 1.5 eV to 4 eV, attributed by Dean (1965) to electron-hole recombination at closely associated donor-acceptor pairs. Wight et al (1971) have shown that the characteristic infra-red emission in the region 0.7 eV to 1.8 eV, which peaks at about 1.25 eV, is attributable to the recombination of free holes and electrons on the platelets of such diamonds.

Type Ib diamond has two characteristic emission features. The first consists of a zero-phonon doublet at 1.4 eV, and phonon assisted structure associated with it to lower energies. Dean (1965) suggested this emission arose from the decay of indirect excitons bound at ionized isolated nitrogen donors. Hopfield (1964) has shown, however, that the exciton binding energy is small, if not zero, at an ionized donor, if the electron-hole mass ratio is close to unity. In addition, Wight et al (1971) found no thermalisation of the 1.4 eV doublet, and this, coupled with the temperature dependence of the energies of the doublet lines led Wight et al to suggest that the observed transition is between two bound electronic states of the nitrogen donor, and that the zero-phonon splitting is produced by a splitting of the ground state. Type Ib

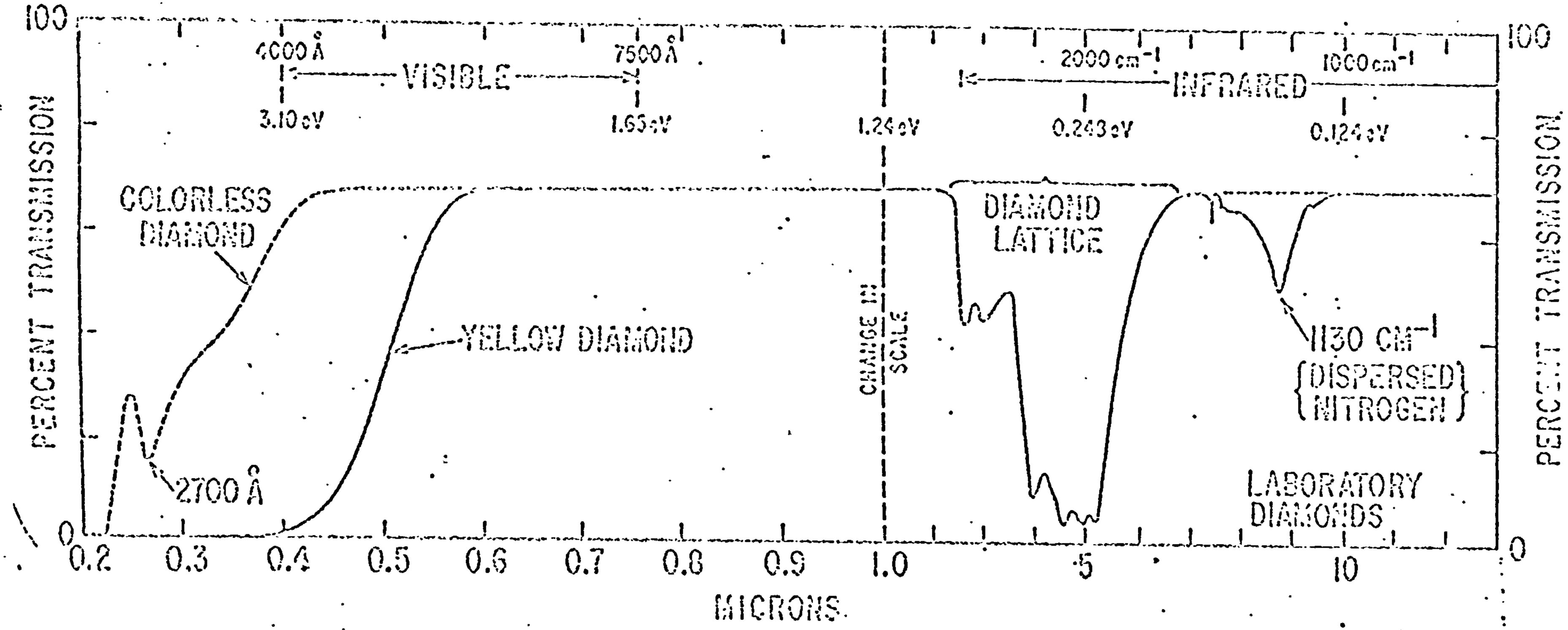

100
PERCENT TRANSMISSION
4000 Å
VISIBLE
7500 Å
3.10 eV
1.65 eV
1.24 eV
2000 cm⁻¹
INFRARED
1000 cm⁻¹
0.248 eV
0.124 eV
COLORLESS DIAMOND
YELLOW DIAMOND
2700 Å
CHANGE IN SCALE
DIAMOND LATTICE
1130 CM⁻¹ {DISPERSED NITROGEN}
LABORATORY DIAMONDS
0
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
5
10
MICRONS

FIG. 1.1

diamond also exhibits an emission band between 1.5 eV and 3 eV attributable to donor-acceptor pair recombination.

## Sec. 1.4 Type II diamond.

Type IIa diamond consists in the main of diamonds having small but measurable quantities of nitrogen, and which exhibit weak, but characteristic, ultra-violet absorption. Such diamonds are of value in the study of the intrinsic diamond lattice.

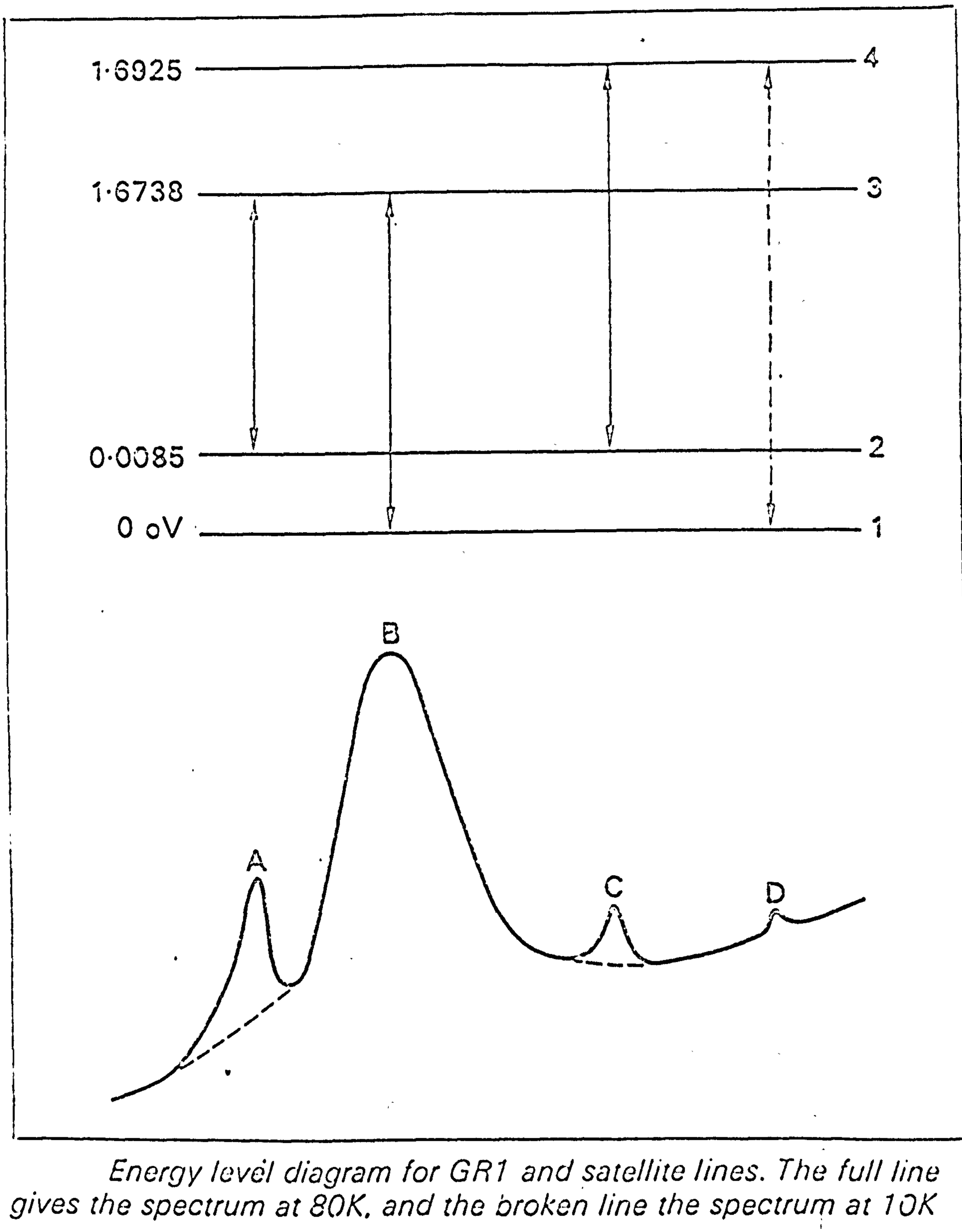
Experimental investigations by Custers (1952, 1954) revealed some type II diamonds to be semiconducting, thereby forming a distinct group, now classified as type IIb diamond. The p-type behaviour of such crystals was demonstrated by Brophy (1955) who, from Hall effect measurements, calculated the ionisation energy of the acceptor centre to be 0.35 eV. Hardy et al (1962) studied the optical absorption associated with the acceptor centre and deduced a similar value for this energy. Collins and Lightowlers (1968) studied optical absorption and photoconductivity associated with the acceptor and derived an ionisation energy of 0.37 eV. These values are in agreement with those calculated by Austin and Wolfe (1956) from electrical conductivity measurements. Dean (1965) derived a similar result from luminescence measurements whilst Dean et al (1965) showed that such diamonds contained mainly the acceptor centres and partially compensating deep nitrogen donor of energy about 3.9 eV. A great deal of conflicting evidence concerning the chemical nature of the acceptor centre has resulted in its being attributed to boron (Lightowlers and Collins, 1976), the optical absorption produced thereby showing a continuum from 0.37 eV to the visible region and producing the blue coloration

characteristic of such diamonds. Type IIb diamonds do not, however, exhibit the ultra-violet absorption shown by type IIa diamonds.

Sec. 1.5 Radiation damage in type I diamond.

It has been shown by du Preez (1965) that if electrons of energy in excess of about 300 keV impinge upon diamond, atoms in the lattice may be displaced, resulting in the formation of vacancies and interstitials. The passage of electrons may also cause modifications of the charge states of lattice defects.

The bombardment of types Ia, Ib, and IIa diamond by electrons readily results in the production of the GRI absorption/emission system (Clark et al 1956a) characterized by a zero phonon transition at 1.673 eV and temperature dependent satellite structure near this transition. The system is produced in type IIb semiconducting diamond only after sufficient electrons have penetrated the lattice to compensate for the p-type nature of this form of diamond (Dyer and Ferdinando 1966). The absorption system, and a proposed energy level scheme, originally due to Clark and Walker (1973) are shown in fig 1.2. Mitchell (1967) postulated the donor nature of the GRI centre, and as a result, it was considered to be either negatively charged or electrically neutral. Consideration of the low mobility of the centre, and of corresponding work on silicon by Watkins (1965), led Mitchell further to suggest that the centre was a vacancy. The energy level scheme of Clark and Walker resulted from a study of the behaviour of the system under uniaxial stress, such behaviour being consistent with that expected of a neutral vacancy. It has recently been suggested by Davies (1976),




*Energy level diagram for GR1 and satellite lines. The full line gives the spectrum at 80K, and the broken line the spectrum at 10K*

FIG. 1.2

however, that certain of the stress splitting patterns produced by these authors may have been caused by misallignment of stress axes, thus casting doubt upon the interpretations at present made of the behaviour and nature of the centre.

All nitrogen containing diamonds, upon subjection to radiation damage produce the NDI centre, characterized by a zero phonon transition at 3.149 eV at 80K (Pringsheim et al 1952), and phonon assisted structure to higher energies. The system is observed only in absorption and its production is only accomplished if the radiation damage is accompanied, or followed, by a rise in specimen temperature to about 250°C, or rather less in the case of type Ib diamond. The need for a rise in temperature was interpreted by Dyer and du Preez (1965) as evidence for an interstitial atom, produced by the irradiation, overcoming an energy barrier to combine with the dominant form of nitrogen impurity (then believed to be platelets in type Ia diamond, and isolated substitutional atoms in type Ib diamond). The energy barrier was considered to be lower in type Ib diamonds, thus necessitating rather lower temperatures. Davies (1969) has observed, however, that there are two reasons for questioning the validity of this interpretation. Firstly, it is doubtful whether the aggregates [platelet + interstitial] and [isolated nitrogen atom + interstitial] would produce the same optical systems, as is found to be the case. The likelihood of at least two distinct forms of nitrogen in type Ia diamond casts further doubt upon this interpretation. Secondly, the NDI centre has been shown by Davies (1969) to exhibit Td symmetry which is incompatible

with the above aggregates. Davies has hence suggested that the NDI centre is an interstitial nitrogen atom, the activation energy being attributed to an exchange between a carbon interstitial produced during irradiation and a nitrogen atom. The barrier to such an exchange is lower when the nitrogen atom is isolated than when it is one of a cluster of such atoms in the A and B forms of type Ia diamond.

Diamond also exhibits cathodoluminescence associated with radiation damage. One such system consists of a zero phonon transition at 3.188 eV along with phonon replicas to lower energies. The system was observed by Ralph (1960) and was considered to be the emission analogue of the NDI absorption system. Davies and Lightowlers (1970) have shown the zero phonon lines to be distinctly different, and found no correlation between NDI absorption strength and 3.188 eV emission. The occurrence of the system in all diamonds suggests it is associated with an intrinsic defect.

A second emission system, also apparently related to an intrinsic defect is that having a zero phonon transition at 2.155 eV. This system was observed by Wight (1968) in a study of radiation damage and was found to increase in emission intensity during cathodoluminescence studies. Davies (1969) suggested the growth of such emission was caused by either a movement of certain radiation damage defects by the electron beam used in cathodoluminescence studies, thereby producing 2.155 eV centres, or, alternatively, by a charge redistribution promoted by the electron beam. Davies observed an electron energy of about 10 keV as being the threshold for stimulation of the emission, which is energetically consistent with

both postulates. The system is presumably not produced during irradiation by 2 MeV electrons during the primary irradiation of the diamond because of the low electron beam densities (ca. 0.4 $Am^{-2}$) used therein, compared with those used in cathodoluminescence studies (ca. 40 $Am^{-2}$). Also, 2 MeV electrons, having greater penetration depth, produce less ionisation per unit volume. The lack of absorption associated with the 3.188 eV and 2.155 eV emission systems suggest either very low oscillator strengths of the transitions involved, or that the transitions occur between excited states of the centres concerned. Absorption by the 2.155 eV system has recently been observed using the technique of luminescence excitation, thereby establishing the low oscillator strength of this transition (M. Hamer, private communication).

Sec. 1.6 Annealing of radiation damage in type 1 diamond.

The work of du Preez (1965) on the annealing of radiation damage in type Ia diamond was interpreted in terms of there being one form of nitrogen in such diamonds, the platelet form. It has been seen in section 1.3 that the impurity induced vibrational spectra of type Ia diamond can be described in terms of two nitrogen forms, A and B, each being different from the platelets. Thermal annealing of type Ia diamond produces two major, nitrogen dependent, absorption/ emission features. These are designated the H3 and H4 systems (Clark et al 1956b) having zero phonon transitions at 503.2 nm and 496.5 nm respectively. These systems are shown in fig. 1.3 due to Crossfield (1973). It has been shown by Davies and Summersgill (1973) that if a given defect, upon thermal annealing, migrates through

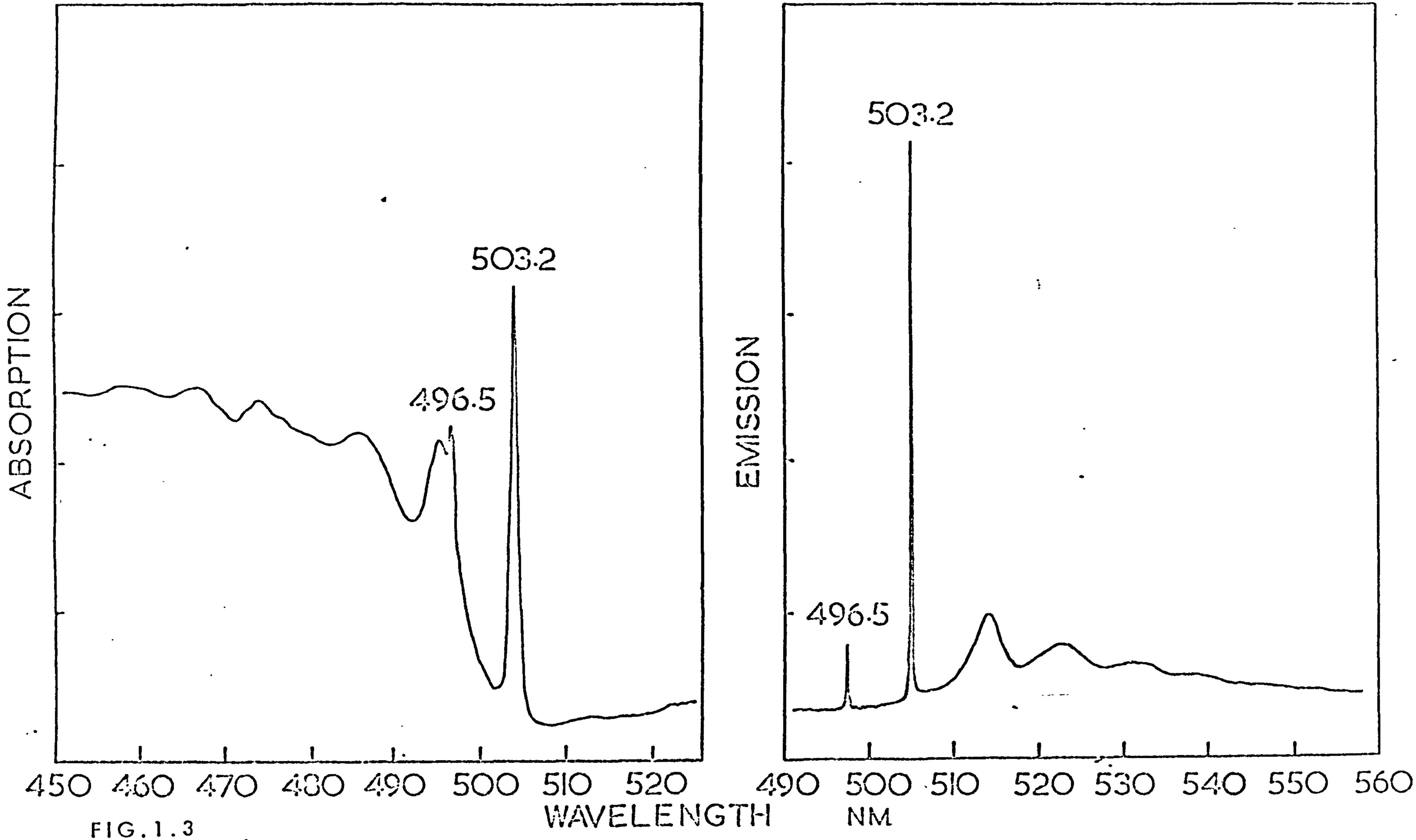
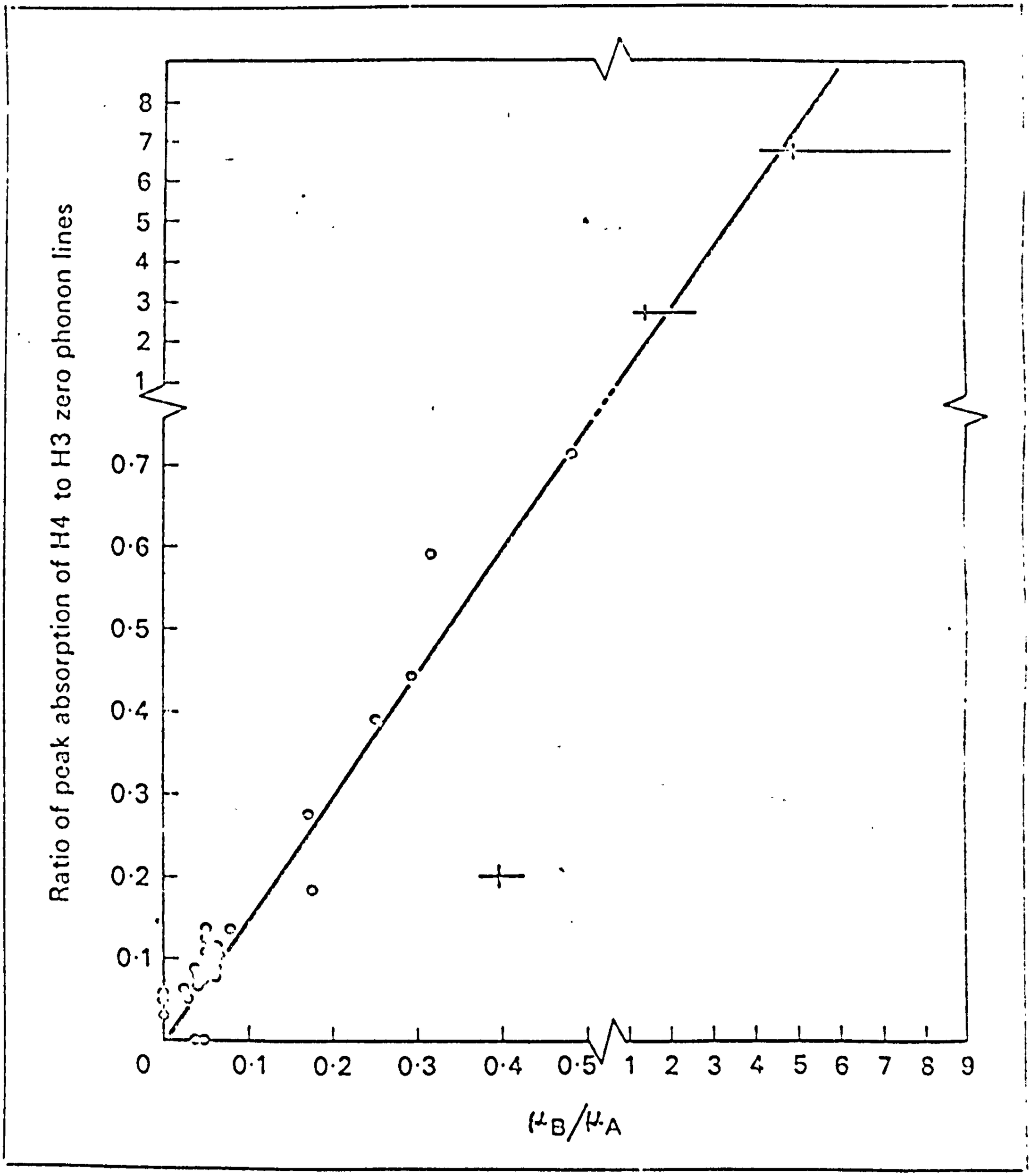

ABSORPTION
503.2
496.5
450 460 470 480 490 500 510 520
WAVELENGTH
EMISSION
503.2
496.5
490 500 510 520 530 540 550 560
NM

FIG. 1.3

the diamond lattice until trapped at the A or B forms of nitrogen, thereby producing H3 and H4 centres, then the ratio of the strengths of the H3 and H4 systems i.e. $\mu_{H3}/\mu_{H4}$ should be proportional to the ratio of the numbers of A and B centres present before annealing. This relationship should hold provided no preferential trapping of the defect at A or B, or other, centres takes place. The ratio of the concentrations of A and B centres is proportional to the ratio of infra-red absorption coefficients associated with the centres i.e. $\mu_A/\mu_B$. The results of such a correlation are shown in fig. 1.4 (Davies and Summersgill) and good agreement is seen to exist between the two ratio quantities involved. The results thus suggest a single radiation damage defect migrates during annealing, and is trapped at A and B nitrogen centres, producing H3 and H4 centres. Extending the results of du Preez (1965) it thus appears that the GRI centre is the defect involved in production of the H3 and H4 centres in type Ia diamond.

In both natural and synthetic type Ib diamond, the major product of annealing of radiation damage is a vibronic system having a zero phonon absorption line at 1.945 eV (du Preez 1965). This feature is seen in fig. 1.5, due to Davies and Summersgill (1973), and by analogy with type Ia diamond, was considered by du Preez to be produced by the trapping of GRI centres at isolated nitrogen substitutional sites. This interpretation is in agreement with that of Davies and Hamer (1976), derived from a study of the symmetry properties of the 1.945 eV system.

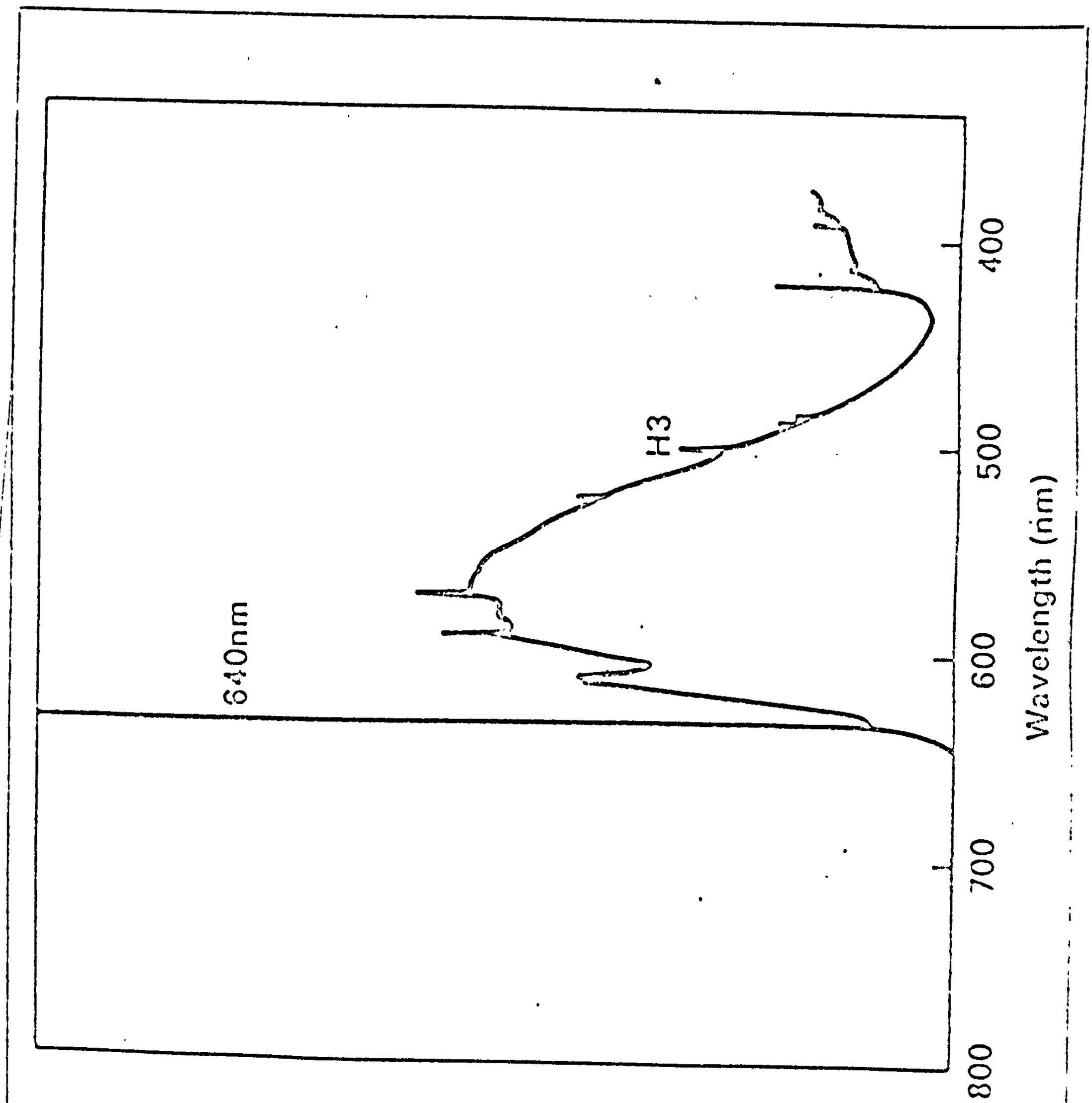
The above interpretations will be discussed in more detail in sec. 5.2.2 of this work.




*The H4 and H3 zero phonon line strengths produced in a diamond by irradiation and annealing are present in a ratio proportional to the ratio of B to A nitrogen*

FIG. 1.4

FIG. 1.5 The 640 nm Absorption System in Type Ib Diamond



## Sec. 1.7. Conclusion

It has been seen that the properties of type I diamond can be considered in terms of the relevant form of nitrogen impurity in such diamonds. At the present time no comprehensive survey of natural and synthetic type Ib diamonds has been made with a view to relating the products of radiation damage to known impurities in the lattice. Ambiguities in the interpretation of annealing of type I diamond, particularly in view of the present interpretation of the NDI centre give rise to the need for a further investigation into this process. It was these two major topics which provided the rationale for the present work.

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# Chapter 2

## Experimental

### Sec. 2.1 Introduction.

This chapter deals with the experimental apparatus and techniques employed during the course of the measurements, for which the results are reported in subsequent chapters of this thesis. The first series of measurements consisted of a survey of the optical properties of synthetic diamonds before and after radiation damage had been caused by 2MeV electrons impinging upon such diamonds. The experimental detail of these measurements comprises sec. 2.2. The techniques used for the measurements of the temperature dependence of a hitherto unreported radiation damage system are discussed in sec. 2.3, whilst sec. 2.4 describes the measurement of the results of annealing natural type Ia and Ib diamonds.

Radiation damage was produced in all the natural and synthetic diamonds investigated by subjecting the diamonds to bombardment by 2MeV electrons, using beam current densities of typically $0.2Am^{-2}$ for periods of typically 3 hours, or longer as required. The irradiation was performed by means of the Van de Graaf Generator of A.E.R.E. Harwell, the diamonds being embedded in the surface of a mound of indium held in a 1" diameter copper block of approximately 0.4" height. The copper block was in turn held in good thermal contact with a water cooled brass mount positioned at the aperture of the electron accelerator in such a way as to facilitate maximum charge falling on the assembly.

## Sec. 2.2 Measurement of optical absorption and emission in synthetic diamonds.

The measurements, for which the results are reported in chapter 3, can conveniently be considered to fall within 4 energy ranges viz:-

a) 120 meV to 180 meV (10$\mu$m to 7$\mu$m) approximately

b) 0.6 eV to 1.70 eV (2$\mu$m to 730nm) "

c) 1.70 eV to 3.0 eV (730nm to 400nm) "

d) 3.0 eV to 6.0 eV (400nm to 200nm) "

The apparatus and techniques employed for measurements in the above energy ranges will now be discussed separately.

a) Synthetic diamonds show absorption in the energy range 120 meV to 180 meV as a result of the nitrogen-induced one-phonon vibrational mode (Dyer et al, 1965). The absorption of radiation by synthetic diamonds in this region was studied by means of a Perkin Elmer Model 99 f/4 monochromator, equipped with a NaCl prism, and thermocouple detector. Radiation passing through the sample and entrance slits makes a double pass of the prism by means of a Littrow mirror. An A.C. signal is produced by a rotating mechanical chopper and rectification of this signal is brought about by a set of contacts touching the rotating cam attached to the chopper.

Because the synthetic diamonds were of such small dimensions ($\sim$1mm), it was not practicable to simply suspend them before the entrance slits of the monochromator, as insufficient radiant energy could be induced to fall on such samples when held in this manner.

This difficulty was avoided by making use of the double Cassegrain infra-red microscope shown diagramatically in fig. 2.1, taken from Collins (1967). In this mode, each specimen was held, firmly fixed by a surround of indium, in an appropriately sized hole in a copper strip of dimensions 5mm x 2mm x 0.5mm, which in turn was clamped to the adjustable cradle between the mirrors of the microscope. Referring to fig. 2.1, radiation from the 3mm diameter Nernst filament A was focussed via mirrors $r_1$ and C, onto sample B which could be moved, by means of adjustment screws, along the axis of mirrors C and D, or in vertical and horizontal directions perpendicular to this axis. Radiation passing through B was then refocussed onto E, the entrance slits of the monochromator, by suitable adjustment of $r_2$ and D.

A further difficulty arose during the measurements as a result of absorption produced by the atmosphere in this spectral region, thereby distorting the true diamond absorption. This was circumvented by encasing both monochromator and microscope, after adjustment of sample position, in a perspex cover through which dry, pure nitrogen was passed during the entire measurement. Such a modification was found to reduce atmospheric absorption to negligible amounts after approximately one hour. However it was found that the calibration of the monochromator was affected by the NaCl prism being subjected to fluctuations of temperature. This effect was annulled by passing the nitrogen gas mentioned above over a heater and thermostat, thereby holding the temperature of the entire assemblage at 34°C throughout the measurement. (Collins 1976)

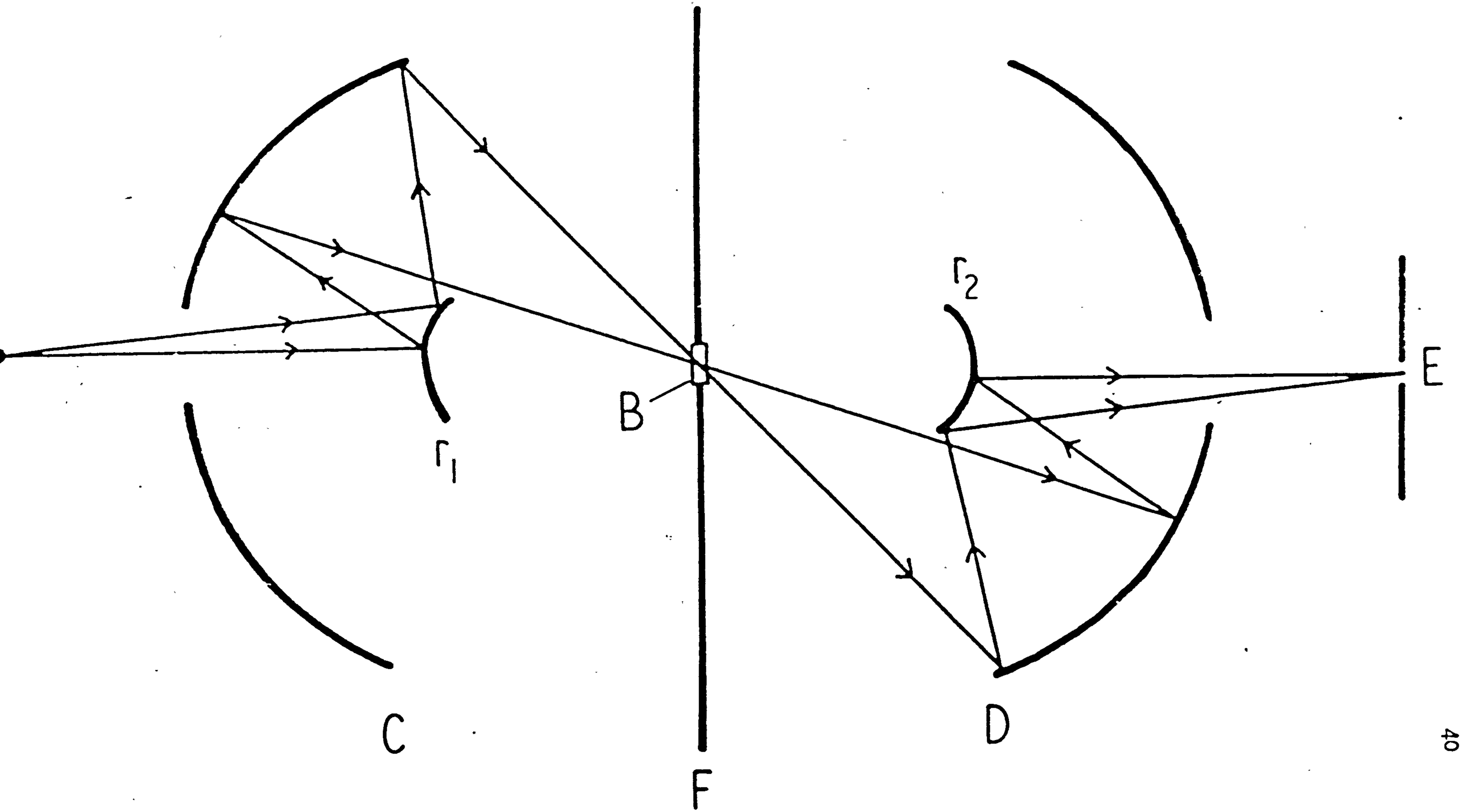


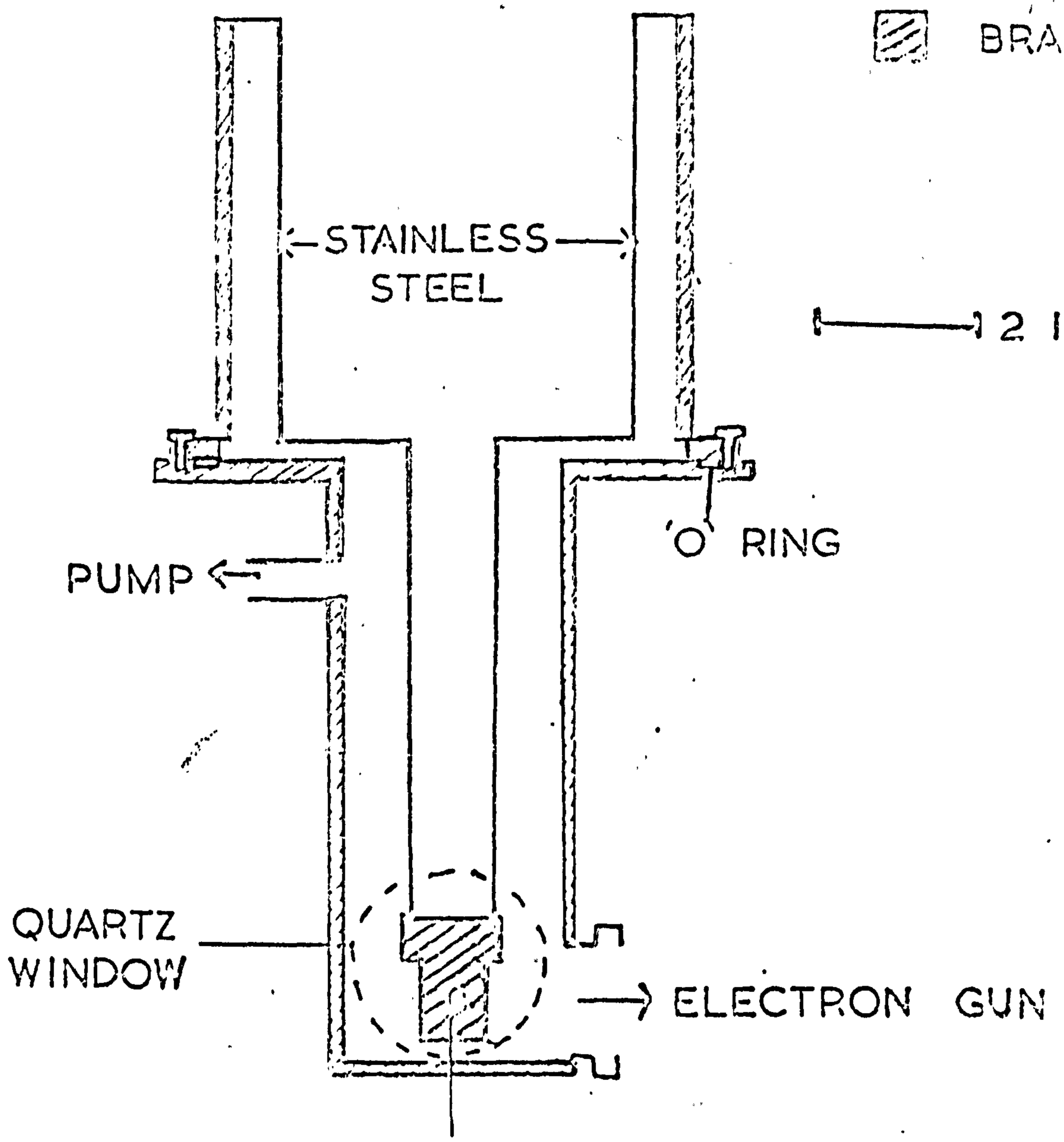

FIG.2.1 Infra-Red Microscope - Schematic

A major hindrance to the production of noise-free spectra, using the above apparatus, was the decreasing emission of the Nernst filament as the wavelength increased in the 7 - 10$\mu$m region. To compensate for this a motor drive was fitted to the monochromator slits which thus opened at a linear rate with time as the wavelength was scanned. When no sample interrupted the beam this device produced an approximately constant radiation level on the thermo-couple detector of the monochromator, whilst not noticeably impairing the spectral resolution of the instrument in this region.

In this manner, the vibrational spectra of synthetic diamonds were recorded at room temperature. The instrument was calibrated by means of the standard wavelengths of absorption by water vapour, and ammonia.

b) Before dealing specifically with measurements made in the 0.6 eV to 1.7 eV energy region, the cryostat used in this, and higher energy, ranges will be described. This cryostat afforded a convenient method of measuring absorption and cathodoluminescence, along with a quick interchange of specimens.

The cryostat is shown diagramatically in fig 2.2. The specimens to be examined were held in copper mounts as described in section 2.2a, and clamped to the copper tip of the stainless steel cold finger of the cryostat. The cryostat had two quartz windows at either side of the cold finger, and with the sample in the correct position could be used in the absorption mode; light source and monochromator being at either side of the cryostat. An aluminium table with adjustable legs supported the cryostat which could thus be adjusted so as to correctly position samples in the light beam. An appropriate lens system gave the required image reduction and focusing power.




ABSORPTION AND CATHODOLUMINESCENCE CELL

FIG. 2.2

The cryostat further possessed an aperture, with its plane normal to that of the quartz windows, but at the same level, and this aperture provided the site for an electron gun used in cathodoluminescence measurements. In this mode the cold finger was turned through $60^{\circ}$ relative to its position in the absorption mode. The electron beam was thus allowed to impinge upon the samples, whilst avoiding the reflection of light emitted from the electron gun filament onto the monochromator. Such reflection, and emission caused by electrons hitting the indium surrounding the sample, was further reduced by coating the sample mount with matt black paint, which was not affected by low pressures in the cryostat.

Pressure inside the cryostat was reduced to $10^{-5}$ torr using a conventional rotary and diffusion pump system, and addition of the relevant liquid coolant to the reservoir above the cold finger was then found to reduce the specimen temperature to within 2K of the nominal coolant temperature. A speedy interchange of specimens was effected by using a high pressure nitrogen jet to remove the coolant from the reservoir and warm the sample sufficiently for it to be exposed to normal air pressure without ice formation. A complete sample interchange could be carried out in less than 15 minutes by this method.

This completes the description of the cryostat employed in measurements below room temperature and we now turn to a description of the apparatus used with this cryostat in the spectral range 0.6 to 1.7 eV.

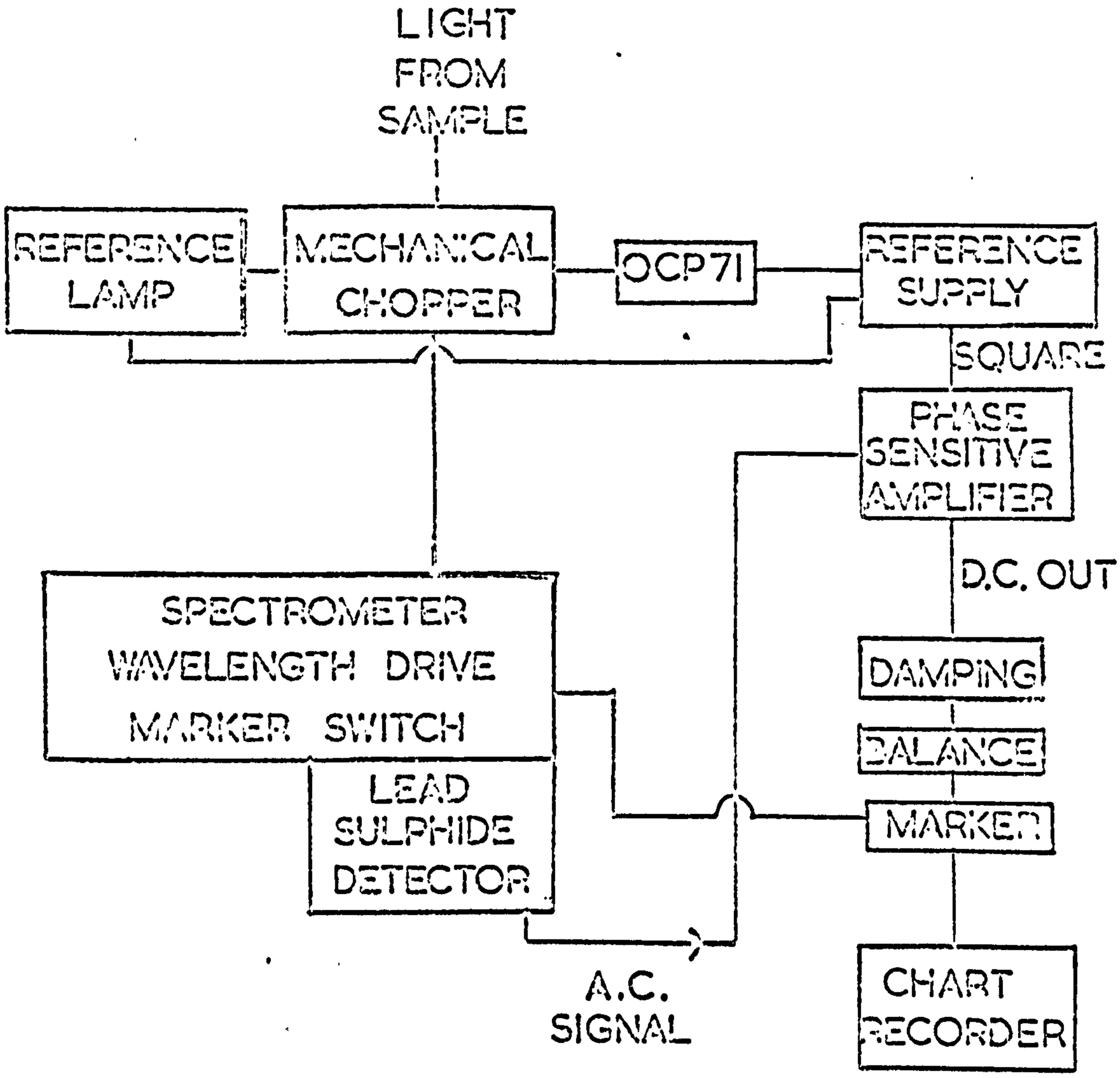
The cryostat was used in conjunction with a Spex 1702 $\frac{3}{4}$ m Czerny Turner f/7.5 grating spectrometer of 1200 grooves/mm and

blazed at a wavelength of 500 nm, giving a spectral resolution of ~10,000. Two glass lenses gave an image reduction and magnification of 3 to 1. The light source used in absorption was a 12 V, 100 watt quartz halogen lamp. The detector used was a lead sulphide cell, cooled to 196K, and phase sensitive detection was employed.

Fig. 2.3 shows a block diagram of the phase sensitive detection system. The reference signal was produced as a result of a mechanical chopper revolving between a pea-bulb and an OCP 71 photo transistor. Radiation passing from sample to monochromator was also interrupted by the chopper. A Brookdeal FL 355 lock-in amplifier was used to amplify the signal produced at the detector.

c) The spectral region 1.7 eV to 3 eV was investigated using the cryostat, lamp (for absorption) and monochromator as discussed above. The detector system used was an EMI 9558 Q photomultiplier tube, linked to a d.c. amplifier. In this region of the spectrum, Chance glass filters were employed to isolate unwanted spectral orders and glass achromatic lenses employed for image reduction.

d) The region 3 eV to 6.0 eV was studied using the cryostat and photomultiplier described above in conjunction with a Jarrell A sh f/10 1 metre Ebert grating monochromator with grating of 30.000 lines/inch blazed at 190 nm. This gave a spectral resolution of 40,000. A DF3H, 0.5A deuterium lamp was used as a light source in these measurements and quartz lenses were employed.




BLOCK DIAGRAM

OF A.C. DETECTION SYSTEM

FIG. 2.3

The electron gun used in cathodoluminescence measurements, with the cryostat described above, was originally used as an electron beam welder and is shown in fig. 2.4. The gun has been described by Collins (1967), and employs electrostatic beam deflection and magnetic focussing with a filament and bias supply shown in fig. 2.5. Electron energies of up to 20 keV could be obtained from a Brandenburg power supply, with beam currents of up to 100$\mu$A .

Spectrometer calibrations in the region 0.6 eV to 4.2 eV were carried out by means of a standard mercury discharge lamp, using the line calibrations of Zwerdling and Theriault (1961).

The absorption spectra recorded in the spectral regions described above were calculated as follows. The signal produced with the sample interrupting the light beam was recorded and is referred to as $I_t$. The sample was then removed and the spectral distribution of the lamp emission recorded. This latter signal is referred to as $I_o$. The quantity $\ln(\frac{I_o}{I_t})$ was then calculated at appropriate energy intervals, depending upon the spectral region under investigation. The majority of samples were of irregular thickness, thus not allowing accurate determination of absorption coefficients, although values accurate to within a factor of 2 or 3 were usually possible. Absorption spectra were normalised to show zero absorption at their lowest point or at some point of known zero absorption.

The cathodoluminescence spectra recorded are not corrected for the spectral responce of the equipment.

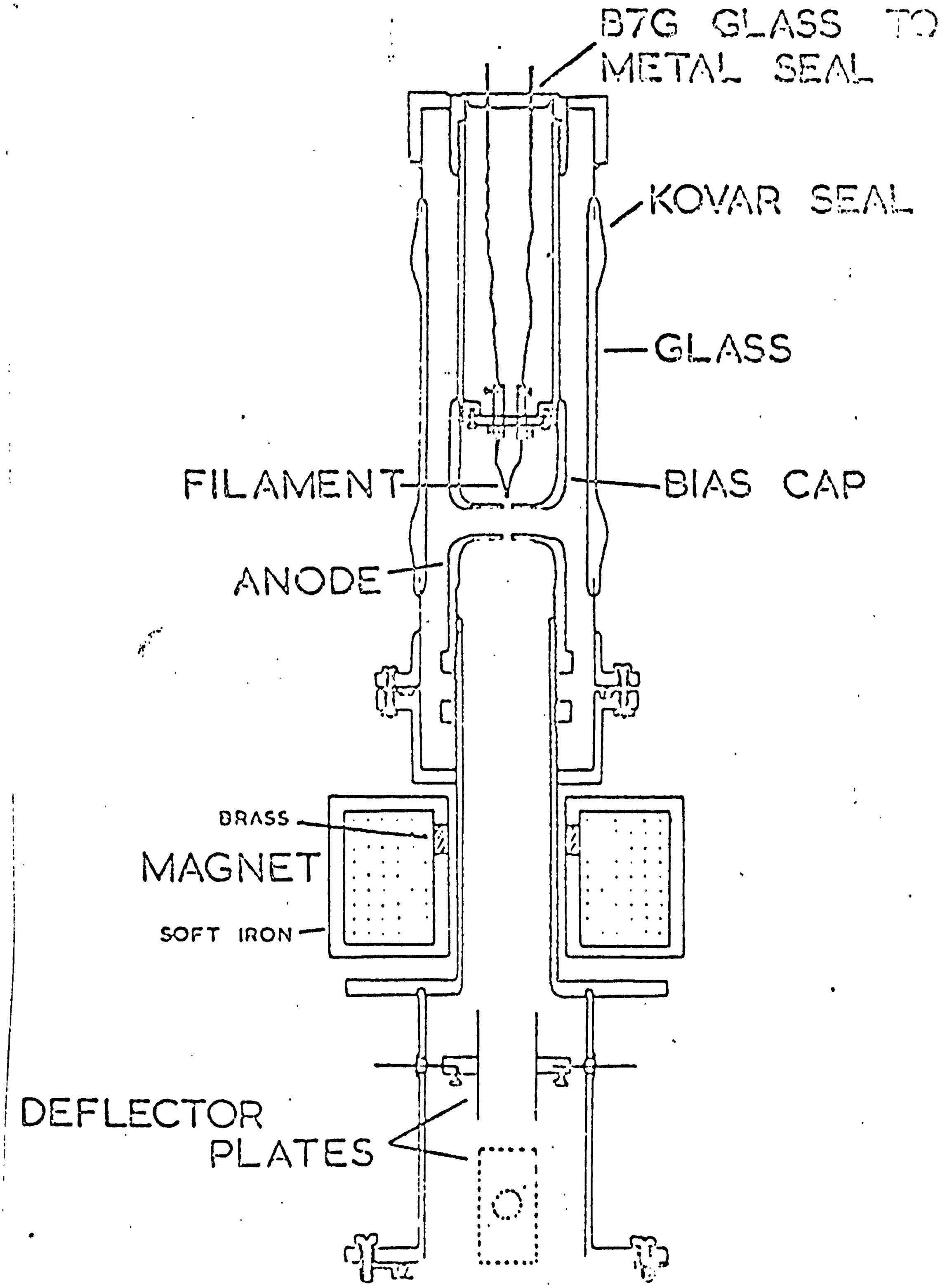



FIG. 2.4

ELECTRON GUN

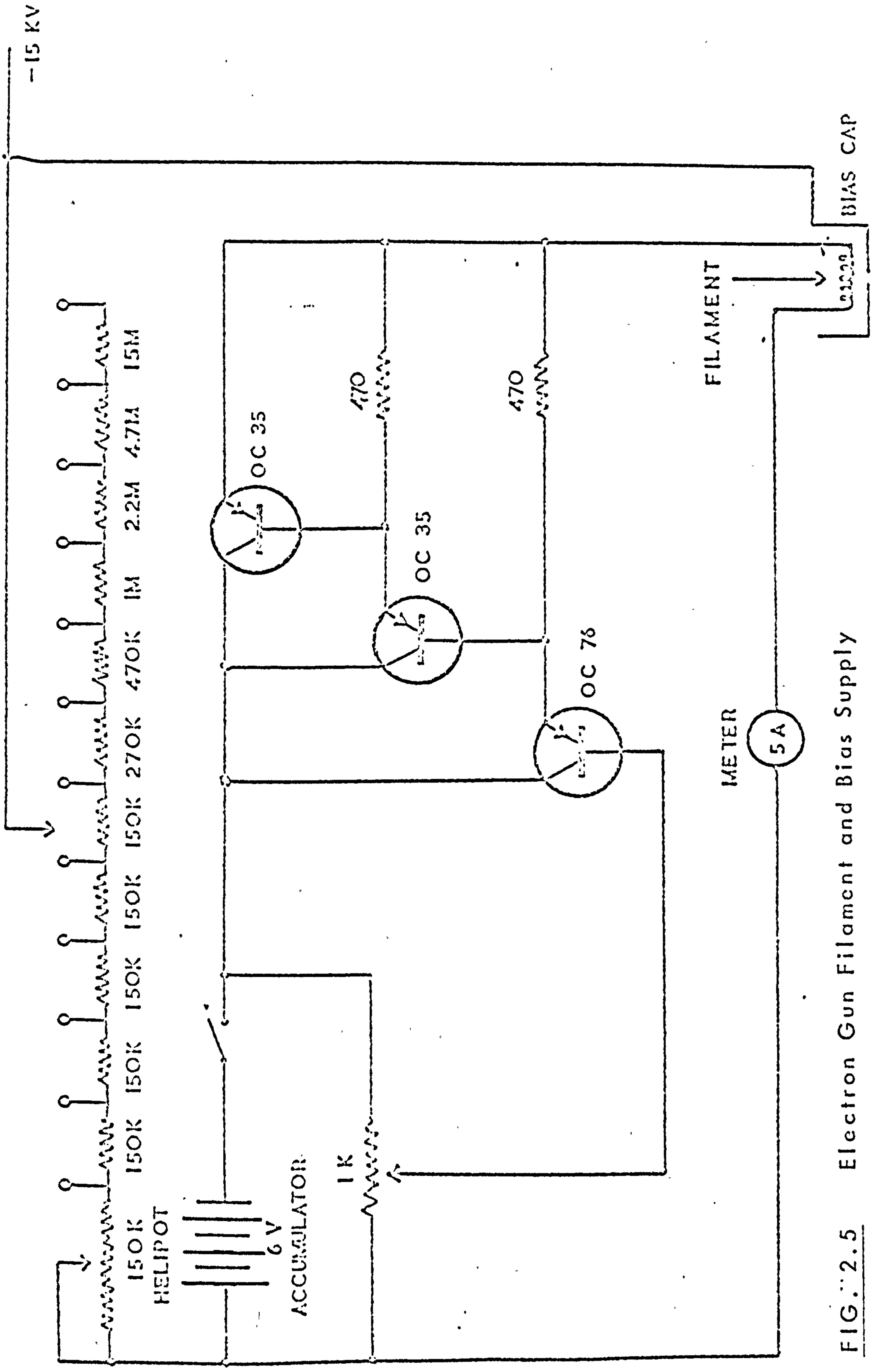



FIG. 2.5 Electron Gun Filament and Bias Supply

## Sec. 2.3. Measurements upon the temperature dependence of the 2.367 eV zero-phonon line.

Chapter 4 reports the results of measurements of the temperature dependence of the 2.367 eV zero phonon line, and of the optical bleaching of this line. The synthetic diamonds used were held in mounts as described in sec. 2.2(a). The natural type Ib diamond investigated for evidence of this line was of dimensions 3mm x 3mm x 1mm, and was placed in an aperture in a 10mm x 10mm x 0.5mm copper plate, with a similar plate on either side. Their outer plates each had a 1mm diameter hole in their centres, overlapping the diamond. The 3 plates were tightly screwed together, as a result of which the same portion of diamond was always monitored, the effect of inhomogeneities being reduced by examination only of such a small area.

The temperature dependences of optical bleaching, and of zero phonon lines, were investigated using a glass double dewar, in which the desired sample temperature was achieved by balancing the effect of a small heater, attached to the tip of the cold finger to which a sample was attached, and the cooling effect of cold gas passed over the sample. The cold gas was produced by heating a carbon resistor suspended in one of the compartments of the glass dewar, containing liquid helium or liquid nitrogen. In this way temperatures could be stabilised to within 1K between 5K and 150K.

The monochromator used in this investigation was a Hilger Monospek f/10 grating spectrometer with a grating having 1200 grooves/mm blazed at 500nm. An EMI 9558 photomultiplier and. d.c. amplifier were used as the detection system, and a 12V, 100 W quartz halide lamp used as light source, with a system of glass lenses.

## Sec. 2.4 Measurements on the annealing of radiation damage in natural type Ia and Ib diamonds.

When undertaking quantitative measurements of the effects of annealing on type Ia and Ib diamonds it was imperative that, after each successive anneal, the same portion of diamond was examined on each occasion. To this end each diamond, being typically several millimetres in dimension, was held firmly in a system of 3 copper plates as described in sec. 2.3, a diamond area of typically 1mm$^2$ being exposed to the light from a quartz halide lamp. A standard glass cold cell fitted with quartz windows held the sample mount, and all spectra were recorded at 77K using the detection system and monochromator of sec. 2.3. A mercury discharge lamp, whose emitted radiation was focussed by a quartz lens onto the diamond, was used to effect charge transfer, as described in chapter 5.

The diamonds were annealed by placing them, still firmly fixed in their copper mounts, into a quartz tube which was subsequently evacuated to about $5 \times 10^{-4}$ torr. The tube was fitted with a chromel-alumel thermocouple clamped to its exterior, in such a way as to make the thermocouple hot junction coincident with the specimen position inside the tube. The cold junction was held at $0^{\circ}$C. and the thermal e.m.f. measured on a digital voltmeter of $10\mu V$ sensitivity. The tube was then inserted into an electrical furnace controlled at a preselected temperature by a Eurotherm control unit. Insertion of the tube caused a temperature drop in the furnace of typically $10^{\circ}$C, which recovered in approximately 1 or 2 minutes. The tube was then fractionally adjusted until the thermocouple indicated that the required temperature had been

attained. Thereafter, the Eurotherm unit controlled the system to within 1°C for as long as was required. The whole process from insertion of tube to attainment of a steady required temperature lasted about $2\frac{1}{2}$ minutes, a time period considered suitably short in view of the fact that no anneal lasted less than one hour, the average being about 10 hours.

After annealing, the diamonds in their mounts were thoroughly washed in acetone so as to remove any foreign matter from the diamond surfaces and apertures through which they were investigated. This washing was carried out in darkness, and subsequently the diamonds were kept in the dark until required for investigation so as to reduce to a minimum charge transfer caused by ambient lighting conditions.

## Chapter 2

## References


| | | | |
|---|---|---|---|
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| Dyer,A.B.,Raal,F.A., du Preez,L.,Laubser,J.H.N. | (1965) | Phil.Mag. | 11, 763 |
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# Chapter 3

# Optical absorption and emission due to radiation damage in synthetic diamonds

## Sec. 3.1 Introduction

This chapter is concerned with a survey carried out on some 15 synthetic diamonds, chosen as being representative of a larger number of such diamonds which were available for study. The specimens examined exhibited a wide range of nitrogen impurity content, and had also been grown in environments containing several different growth catalysts. The diamonds studied were investigated for their properties of optical absorption and cathodoluminescence before and after radiation damage by 2 MeV electrons, with a view to relating any optical features produced by radiation damage to the known impurity content of the diamonds.

The synthetic diamonds investigated were derived from four specific sources, and can be classified as follows.

a) The 71/134 series, being commercial grade industrial diamonds supplied by de Beers Ltd.

b) The SAR 65 series, being commercial grade industrial diamonds supplied by de Beers Ltd

c) The GE 68 series, being synthetic diamonds grown by General Electric Company Ltd., in a nominally nitrogen free atmosphere.

d) Fe Ni, Fe B etc. being industrial diamonds grown with different catalysts, and containing a range of nitrogen concentrations.

The physical dimensions of the above all fell in the range 0.5mm to 2.0mm. We shall now discuss the preliminary measurements carried out on the above diamonds, particularly in order to determine their nitrogen impurity concentrations.

## Sec. 3.2. Optical absorption in synthetic diamonds before radiation damage.

It has been seen in section 1.3 that natural type Ib, and nitrogen containing synthetic diamonds exhibit a characteristic infra-red absorption in the energy region 120 meV to 180 meV (10.3$\mu$m to 6.9$\mu$m). Such absorption is caused by the presence of isolated substitutional nitrogen atoms and was observed in all diamonds studied in the present work, other than those of the GE 68 series which were known to be of low impurity nitrogen content. Fig. 3.1 shows the impurity induced one-phonon absorption observed in specimen Fe Ni/A as recorded at room temperature. It is seen that a broad maximum occurs in the absorption at 140 meV photon energy. The absorption at this energy was found by Chrenko et al (1971) to correlate with the nitrogen content of such diamonds, as determined from electron paramagnetic resonance techniques, and consequently this feature has been used in the present work to estimate the nitrogen content of the synthetic diamonds studied.

In addition to the dominant 140 meV peak, the absorption band in the 125 meV to 155 meV region shows two "shoulders" at 136 meV and 147 meV. These two features were observed in all diamonds in which the 140 meV peak was observed, but their relative absorption strengths were found to be specimen dependent, variations

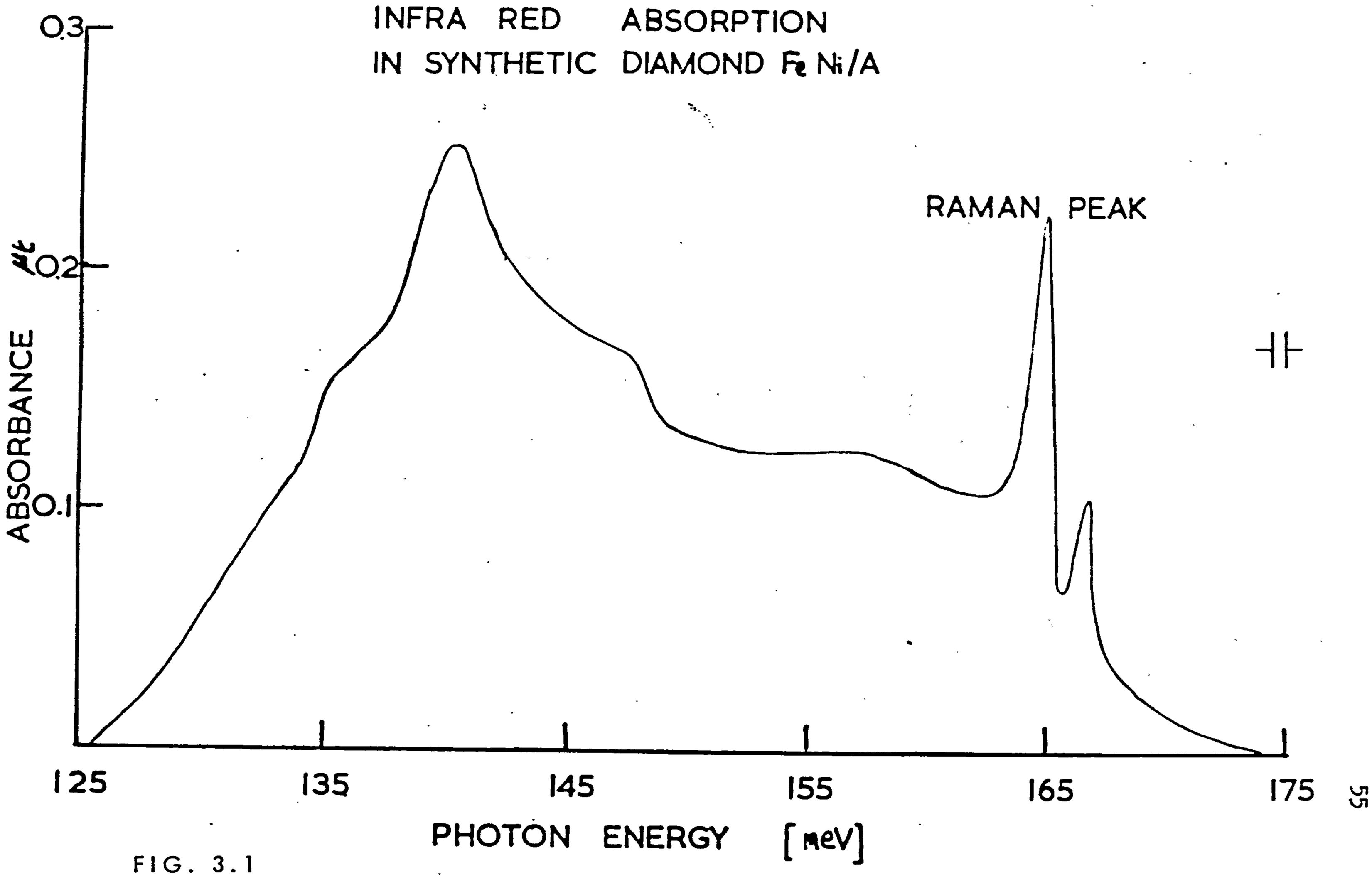
INFRA RED ABSORPTION
IN SYNTHETIC DIAMOND Fe Ni/A
RAMAN PEAK
ABSORBANCE
0.3
0.2
0.1
125
135
145
155
165
175
PHOTON ENERGY [meV]

FIG. 3.1

of up to 7% being observed in their relative intensities. Whilst no pattern was obvious concerning the specimen dependence of this effect, a definite trend was observed concerning the strengths of the 136 meV and 147 meV features relative to the absorption at 140 meV. It was seen that the sequence of catalysts used in the growth of the diamonds viz. (iron and nickel) (iron and cobalt), (nickel), (cobalt), reflects the trend from high absorption to low absorption at 136 meV and 147 meV, relative to the 140 meV absorption. The relative places of (iron and cobalt), (nickel), and (cobalt) in this series have been observed by Charrette (1970), although the latter did not have access to sufficiently large specimens grown in (iron and nickel).

It appears that the use of various catalysts in the growth of synthetic diamonds can lead to partial suppression of certain modes of the impurity induced one-phonon spectrum. No estimates were available of the likely quantities of such catalysts in the diamonds after completion of growth, but catalyst concentrations of up to 0.2% are frequently observed in synthetic diamond, in the form of inclusions. In addition, nickel concentrations of $10^{26}$ $m^{-3}$ have been detected in synthetic diamond by Huggins and Cannon (1962). It is thus unclear whether the behaviour of the 136 meV and 147 meV features depends primarily upon the chemical nature of the catalyst used in growth, or upon the concentrations of catalyst present as impurities in the diamond. However, no spectral features directly attributable to impurities other than nitrogen were observed in the present work, and hence the concentrations of such impurities are probably considerably

lower than those of nitrogen.

The absorption spectrum reproduced in fig. 3.1 also shows sharp absorption peaks at 165.0 meV and 166.7 meV. The former is the perfect lattice Raman energy of diamond. This vibrational mode is disallowed by the symmetry of the perfect lattice, but is allowed in the presence of lattice impurities. This peak was not observed in all the nitrogen doped specimens investigated, and neither was its presence apparently associated with any particular catalyst used during growth of a diamond. The Raman phonon peak was, however, only observed in diamonds of nitrogen content above about 100 p.p.m. Hence, it appears that considerable impurity concentrations are necessary for a measurable absorption at this energy.

The absorption peak at 166.7 meV was also observed in most (but not all) diamonds of relatively high nitrogen content (100 p.p.m.) Absorption at this energy was always found to be accompanied by the Raman peak, although the converse was not found to be true. The strength of the 166.7 meV peak was always found to be rather less than that of the Raman peak, and, because of its energy, it is considered to be a highly localised vibration, centred on an impurity presumed to be nitrogen. The peak is not coincident with the 169 meV absorption shown by Sobolev et al (1967) to correlate with the concentration of platelets in type Ia diamond.

It has been seen in section 1.3 that, in addition to the infra-red absorption in synthetic diamond, Chrenko et al (1971) also demonstrated the presence of absorption at 4.58 eV (270 nm) as being proportional to paramagnetic nitrogen content. In the present work

the absorption at 4.58 eV was too strong in all diamonds, except those of the GE 68 and FeB series, to measure the absorption at this energy. The absorption at 270 nm is shown in fig. 3.2 as recorded for specimen GE 68 / 973 X 3 at room temperature.

From the foregoing infra-red and ultra-violet absorption measurements, the diamonds studied in this survey can be categorised by nitrogen content as follows:-

1) FeNi series, SA 65 series, 71/134 series, being yellow diamonds of nitrogen content in the range 80 - 200 p.p.m.
2) GE 68 series being colourless diamonds of nitrogen content 10 - 30 p.p.m.
3) FeB series, being colourless diamonds of nitrogen content 50 p.p.m.

Sec. 3.3. Cathodoluminescence in unirradiated synthetic diamond.

When excited by 18 keV electrons, all specimens examined, other than those of nitrogen content below about 50 p.p.m. showed the characteristic band of emission consisting of a zero phonon doublet at 1.4 eV and phonon structure at lower energies. The system is shown, with the doublet unresolved, in fig. 3.3 taken from Wight et al (1971), and its occurrence only in synthetic diamonds of high nitrogen content suggests that it may well be a transition at an isolated substitutional nitrogen atom, as postulated by Wight et al.

In addition to the above emission system, the usual band A luminescence centred around 2.2 eV and attributed by Dean (1965) to donor-acceptor pair recombination was observed in all specimens.

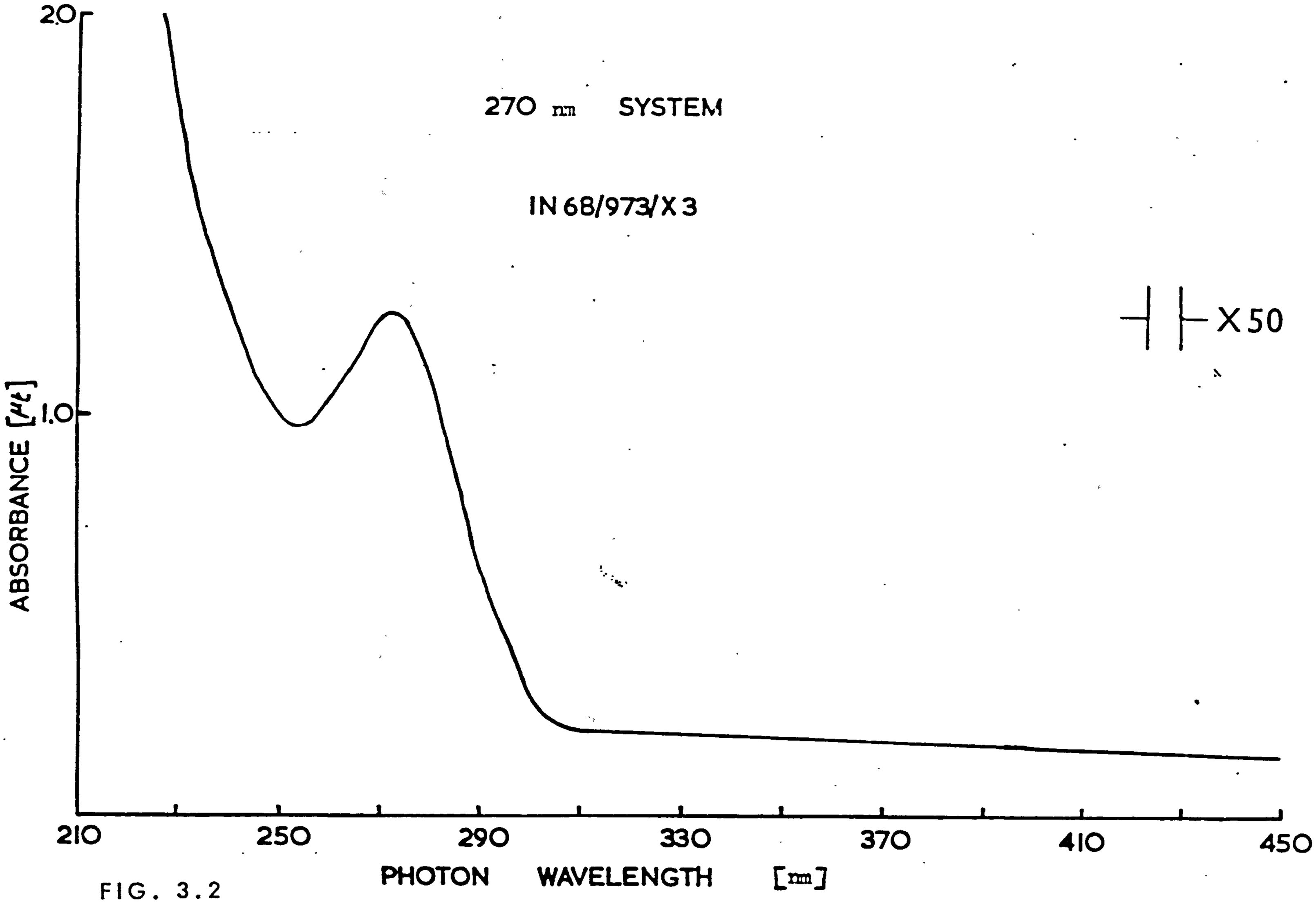
270 nm SYSTEM
IN 68/973/X3
X50
20
1.0
ABSORBANCE [μt]
210
250
290
330
370
410
450
PHOTON WAVELENGTH [nm]

FIG. 3.2

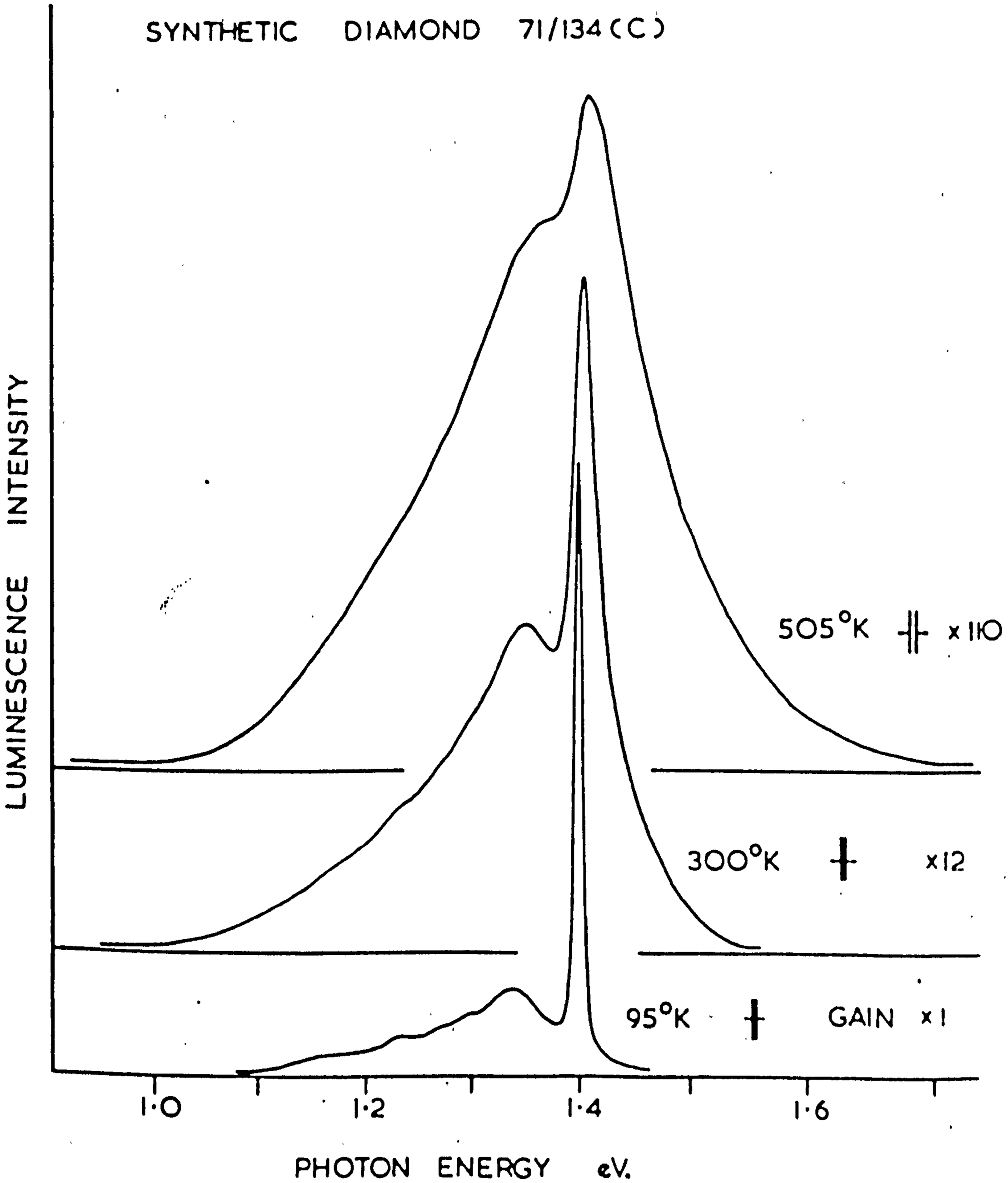
SYNTHETIC DIAMOND 71/134 (C)
LUMINESCENCE INTENSITY
505°K ⫫ x110
300°K ⫫ x12
95°K ⫫ GAIN x1
1·0
1·2
1·4
1·6
PHOTON ENERGY eV.

FIG. 3.3

## Sec. 3.4 Absorption produced by radiation damage in synthetic diamond.

The synthetic diamonds investigated were subjected to radiation damage by 2 Me V electrons at beam current densities of 0.2 $Am^{-2}$ at nominally room temperature for initial periods of 3 hours, followed by longer periods as necessary.

After irradiation, the previously colourless GE 68 and FeB series diamonds, of low nitrogen content, were coloured very pale blue, whilst those of higher nitrogen concentrations were seen to be pale green. All specimens exhibited absorption by the NDI system, with zero-phonon line energy 3.148 eV (Pringsheim et al, 1952). Since this system is known to be formed only after a combination of radiation damage and heating of a diamond to about 250°C it is suggested that the irradiation carried out in the present work was accompanied by beam heating. In addition to the NDI system, all specimens showed absorption by the GRI system (Clark et al 1956), characterized by a zero-phonon transition at 1.673 eV. After the initial 3-hour irradiation, no fine structure was observable in the GRI system, but such structure was detectable after the irradiation dose had been increased by, typically, a factor of 4. This absorption system accounts for the pale blue coloration of the diamonds of low nitrogen content.

Fig. 3.4 depicts a typical absorption spectrum produced by synthetic diamonds of nitrogen content ~ 100 p.p.m., in the photon energy region 1.6 eV to 2.6 eV. The spectrum was recorded after 3-hour irradiation, and at a temperature of 80K, using

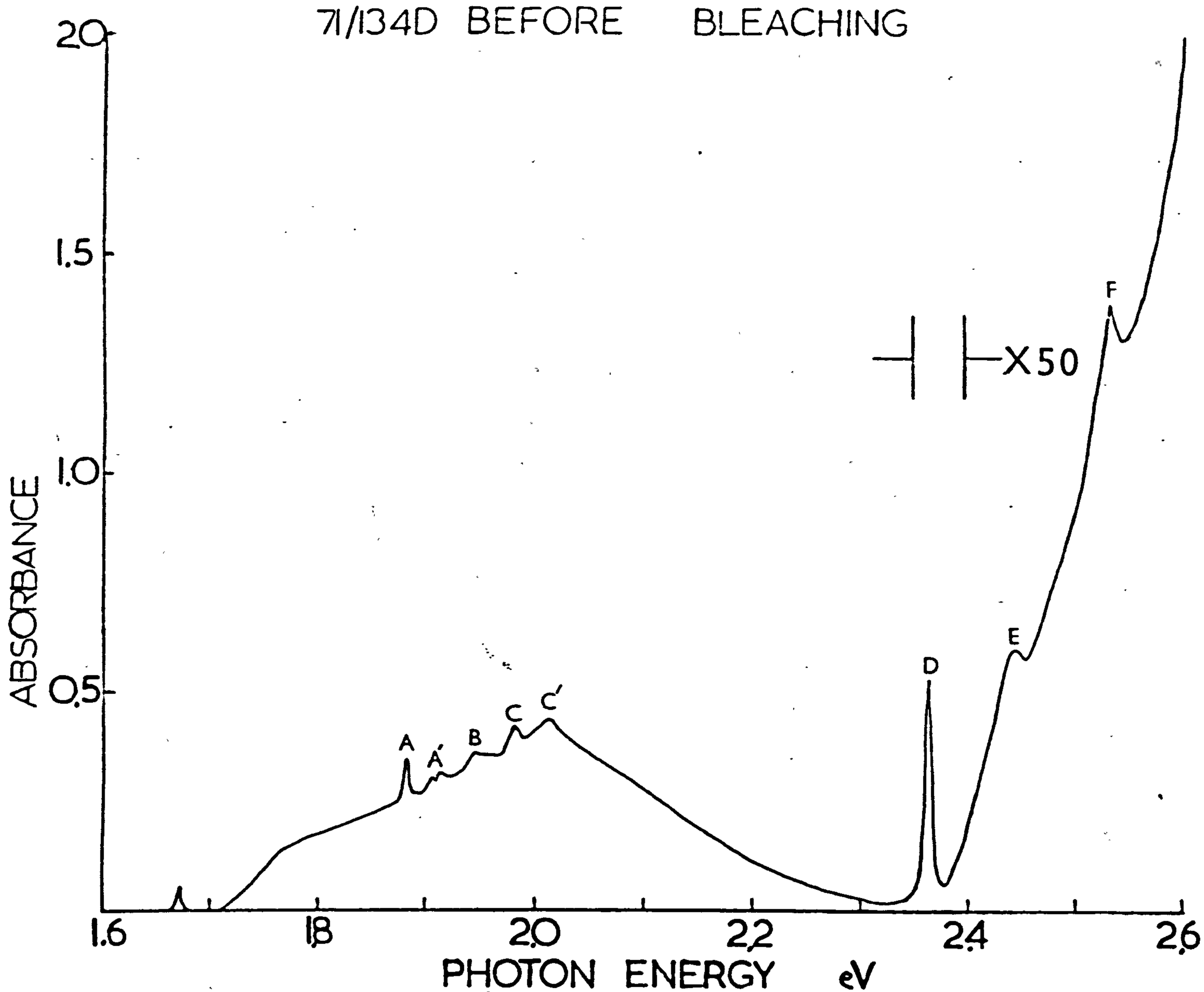
71/134D BEFORE BLEACHING
20
1.5
1.0
0.5
ABSORBANCE
X50
A
A'
B
C
C'
D
E
F
1.6
1.8
2.0
2.2
2.4
2.6
PHOTON ENERGY eV

FIG. 3.4

diamond 71/134D ( nitrogen content 150 p.p.m.). Weak GR1 absorption is seen at 1.673eV, whilst an absorption continuum leads from ~ 2.4 eV to higher energies.

An absorption system, consisting of a peak at 1.883 eV ( designated A of fig. 3.4), and a doublet at 1.906 eV and 1.913 eV ( feature A′ ) is seen in this spectrum , as indeed it was observed in similar spectra recorded for all other synthetic diamonds of greater than 50 p.p.m. nitrogen content. This system has been observed in some, though not all , irradiated natural type 1b diamonds(Davies 1972). The occurrence of this feature suggests it is associated with isolated substitutional nitrogen, as it has not been observed either in previous work, or in a survey of type 1a diamonds presented in chapter 5 of this work. The strengths of features A and A′ were found to increase with radiation dose, but the ratio of absorption by this system to absorption by features C ( 1.979 eV), D ( 2.367 eV) and ND1 (3.149 eV) was not found to depend upon the ratios of any of the dominant features of the infra red one phonon absorption spectrum i.e. those at 136 meV, 140 meV, 147 meV, 165 meV (Raman) and 166.7 meV. Neither was the strength of the system seen to be dependent upon the catalysts used in the growth of the diamonds. It is thus not clear what form the relevant radiation damage centre takes. The system was generally too weak to allow phonon assisted transitions to be detected or for its temperature dependence to be ascertained.

Absorption feature B of fig 3.4 occurs at 1.943 eV , and appears to be related to features A and A′ (Davies 1976), although it also is a weak system.

Feature C occurs at a photon energy of 1.979 eV(Davies 1976),

and also appears in all synthetic diamonds of greater than about 50 p.p.m. nitrogen content, but it does not bear a constant intensity ratio to features A, A', and B. The narrow line width of C (6 meV at 80K) suggests it is a zero-phonon transition.

Feature C', at 2.007 eV, was found to correlate with C, and hence is probably the first phonon replica of C, yielding a phonon energy of 28 meV. The width of C increased to typically 12 meV at room temperature, which is typical of the phonon broadening of many such vibronic systems in diamond e.g. NDI, GRI (Davies 1969). No absorption corresponding to a transition at 1.979 eV was observed in an irradiated natural type Ib diamond investigated during the present work, thus presenting a further complication in the identification of the centre involved.

A zero phonon line, feature D, is seen in fig. 3.4 at a photon energy of 2.367 eV. The line is typically 4 meV wide at 80K, and, again, its occurrence suggests it is dependent upon nitrogen in the lattice. Phonon assisted structure could not be isolated in synthetic diamonds, because of the steeply rising background absorption in this region in those specimens of sufficiently high nitrogen content to show appreciable absorption at 2.367 eV. However, the zero-phonon line, and possible phonon structure, have been observed in natural type Ib diamonds during the course of the present work, and will constitute, in part, the subject matter of chapter 4.

The features designated E and F of fig. 3.4 were observed in all synthetic diamonds, irrespective of nitrogen content.

They occur at photon energies of 2.443 eV and 2.535 eV respectively, having widths of typically 8 meV and 5 meV at 80K. No correlation was observed between the strengths of these lines at a given temperature, and the two lines were seen to have a greatly different intensity ratio in a natural type 1b diamond. In addition, Davies(1976), has reported that the 2.535 eV line does not occur in type 1a diamonds whereas the 2.443 eV line does. The features thus appear to be related to different centres, the 2.535 eV line not being connected with an intrinsic defect, whereas this is possible for the 2.443 eV line. Neither system was found to be enhanced in diamonds of high isolated nitrogen content, and so such centres would not appear to be responsible for the 2.535 eV line.

In addition to the foregoing absorption features, two absorption systems were observed only in diamonds of impurity content below about 60 p.p.m. Fig. 3.5 shows optical absorption in synthetic diamond FeB/C, as recorded at 80K after a radiation dose of $0.2Am^{-2}$ for 3 hours.

Fig. 3.5 was recorded in a spectral region of rapidly changing lamp intensity, and thus slowly varying absorption coefficients caused by phonon replicas of zero phonon lines are not easily separable from the lamp emission profile whilst sharp changes due to the zero phonon lines themselves are easily distinguishable. In addition to the GR1 system at 1.673 eV, and the features E and F at 2.443 eV and 2.535 eV, two lines are seen at 2.010 eV and 2.083 eV. The former line, apparently zero phonon in nature, has a width of 8 meV at 80K and was detected in only two synthetic diamonds. The line at 2.083 eV was seen in all diamonds of low nitrogen content, and was later observed in all diamonds, irrespective of nitrogen content, after annealing. Davies (1976) has reported this feature as occuring in type 1a diamond after irradiation and annealing and it will be discussed further in section 3.6 along with other results of annealing. No further information can be given

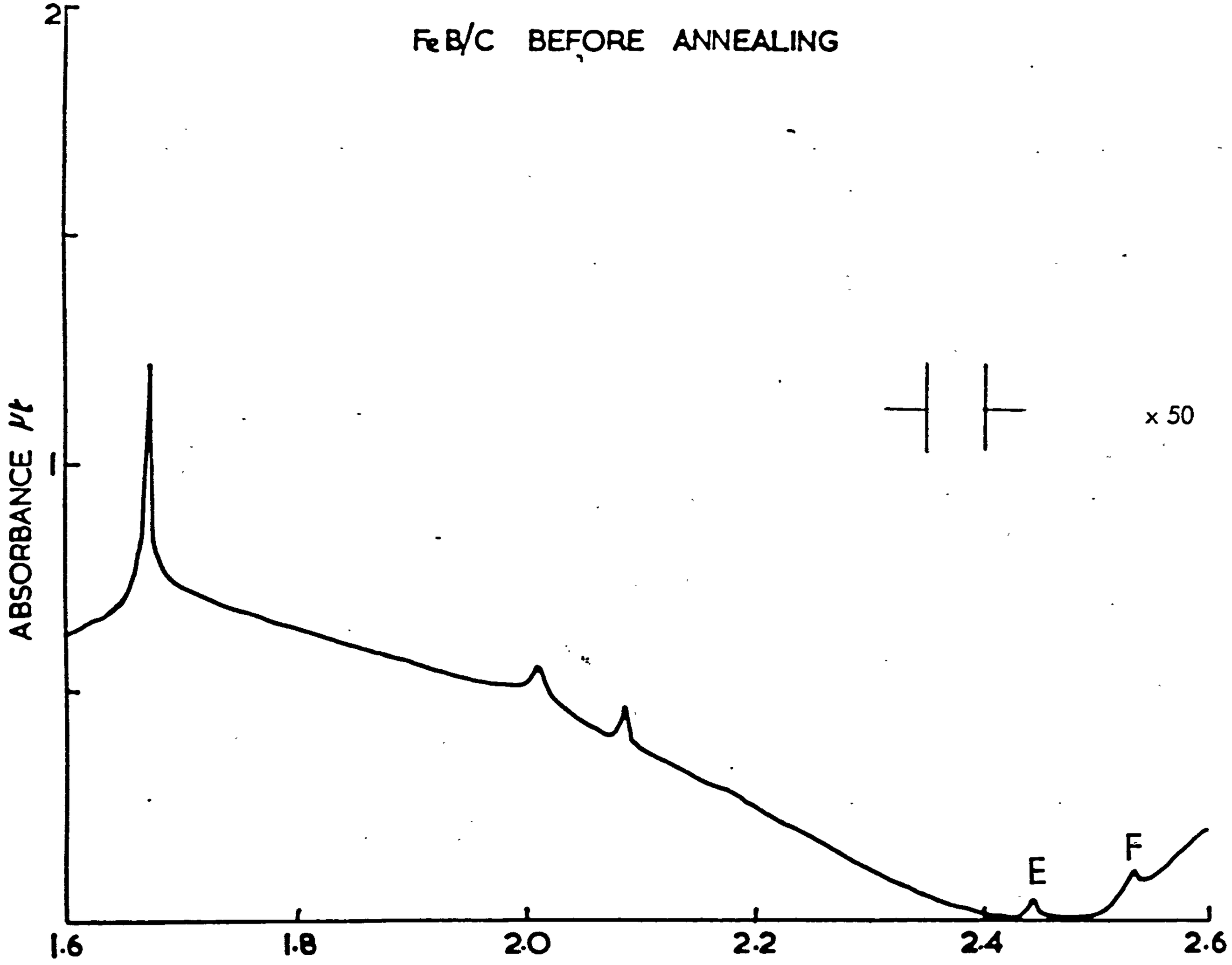
Fe B/C BEFORE ANNEALING
2
ABSORBANCE μt
x 50
E
F
1.6
1.8
2.0
2.2
2.4
2.6
PHOTON ENERGY eV

FIG. 3.5

concerning the 2.010 eV line, other than the observation that the line was not enhanced by subjecting the diamonds concerned to higher radiation doses.

Several new absorption features in the visible spectral region, associated with radiation damage have been reported above. All the specimens investigated were also studied for changes in the infra-red one-phonon absorption spectra. No such changes were detected in any specimen, and it is assumed this was due to the small total charge impinging upon the specimens during radiation damage. The typical charge density associated with the above radiation doses was $4 \times 10^{21}$ electrons $m^{-2}$, and occasionally as high as $1.6 \times 10^{22}$ electrons $m^{-2}$. Radiation induced infra-red absorption has been observed in natural type IIa diamonds by Smith, Hardy and Mitchell (1962), but only after electron doses of $10^{23}$ electrons $m^{-2}$ and above. It thus seems that considerably higher levels of irradiation than those used in the present work are necessary.

## Sec. 3.5 Cathodoluminescence associated with radiation damage in synthetic diamond.

After radiation damage all the synthetic diamonds, irrespective of nitrogen content, were seen to emit an apple-green luminescence when excited by 18 keV electrons. It has been shown in sec. 3.3 that undamaged synthetic diamond shows an emission doublet at 1.4 eV, attributed by Wight et al (1971) to a transition at the isolated nitrogen donor. After radiation damage this system could not be detected in any specimen, suggesting either a

change of the charge state of the nitrogen impurity or production of defects which give rise to more favourable recombination processes. Such defects may be intrinsic or could involve a change of site of the nitrogen atoms e.g. in becoming NDI centres.

After irradiation, all diamonds exhibited a zero-phonon line at 3.188 eV and associated phonon structure at lower energies. In agreement with Davies (1970), the zero phonon energy is distinctly different from that of the NDI absorption system. The zero phonon line and phonon replicas at displacements of 80 meV and 165 meV from the zero phonon line are shown in fig. 3.6, as recorded for specimen Ni(B) (of nitrogen content ~150p.p.m.) at 80K.

All synthetic diamonds of greater than 50 p.p.m. nitrogen content were found to exhibit luminescence as shown in fig. 3.7, recorded for specimen SAR565/7 at 80K. Two lines are seen at 2.595 eV and 2.562 eV, along with a doublet at 2.538 eV and 2.533 eV. This system of lines was first observed by Wight (1968), although he did not report the presence of the 2.595 eV line. This latter line was, however, observed by Davies (1969), who reported the increase in its emission strength relative to the rest of the system as a function of temperature rise. Phonon replicas of the 2.562 eV line and the doublet are seen at 2.440 eV and 2.415 eV respectively, giving a phonon spacing of about 120 meV. Wight has suggested that, since the phonon structure is rather sharp, and of an energy at which the phonon density of states is low, then the phonons are highly localised to the defect responsible for the electronic transition.

Fig. 3.7 also shows weak emission at 2.465 eV, seen in a

3.188 eV EMISSION SYSTEM

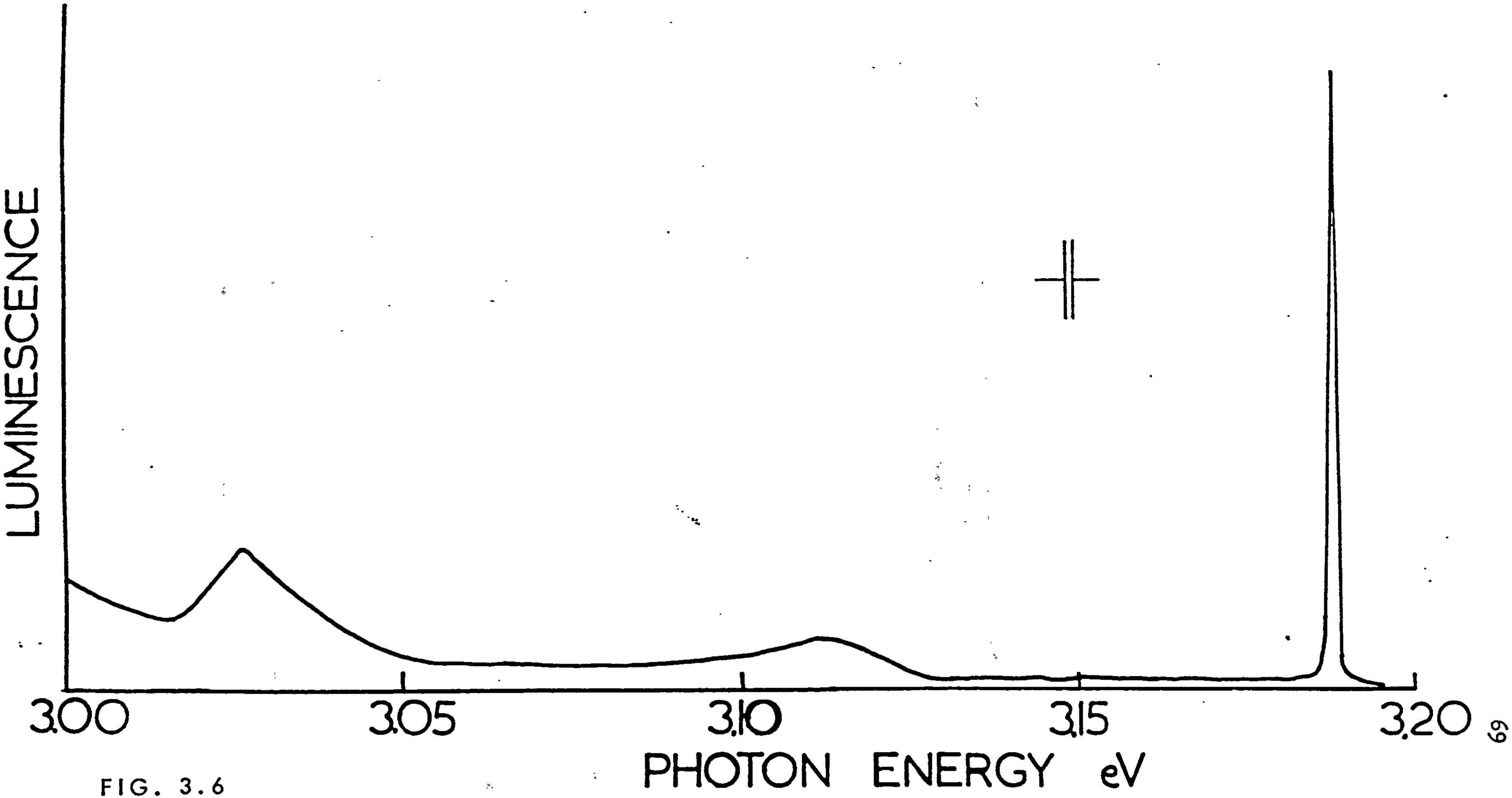


FIG. 3.6

2.562 eV EMISSION SYSTEM

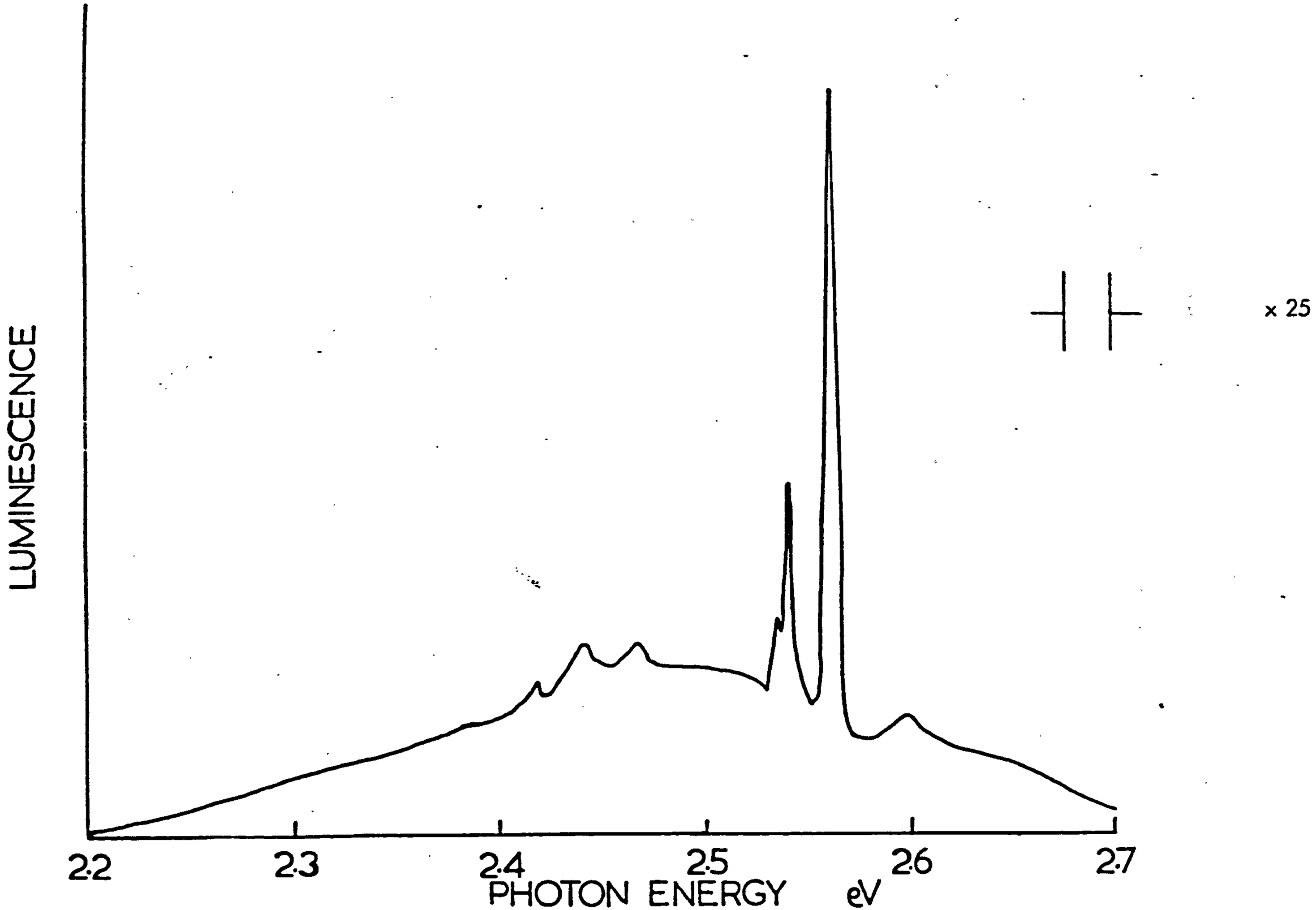


FIG. 3.7

number of specimens of higher nitrogen content. This is the H3 system (Clark et al 1956), produced during annealing of radiation damage in type Ia diamonds, and is attributed in synthetic diamond to localised annealing during cathodoluminescence, associated with small quantities of non isolated nitrogen.

All the synthetic diamonds showed emission consisting of a zero phonon line at 2.155 eV and associated phonon structure (Wight 1968). The system is shown in fig. 3.8 as recorded in specimen $N_i$(B), nominally 80K. The growth of the system during cathodoluminescence experiments has been discussed in sec. 1.5, such growth causing all specimens to glow bright red after several minutes of excitationby18 keV electrons. Such enhancement of the emission was found to be irreversible, suggesting that the electrons produce the system by localised annealing. The emission was found to be generally more intense in diamonds of low nitrogen content, presumably because of the lack of a strongly competitive decay process in such diamonds. The centre involved would thus appear to be intrinsic. Fig. 3.9 shows cathodoluminescence observed in specimen FeB/C. In addition to the 2.155 eV system discussed above, luminescence is seen corresponding to the GRI absorption system at 1.67 eV (Clark et al 1956). As with the 2.155 eV system, GRI emission appeared stronger in specimens of lower nitrogen content. Also shown is an apparent zero phonon line at 1.912 eV (648 nm). This feature was observed in this specimen only, not being seen in similar specimens grown in the same catalytic medium. Emission at an energy close to 1.912 eV has been observed in laser excited emission from natural type Ia diamond by Duncan and Parsons (1970), but no suggestion can be made as to its origin.

A study of the emission of infra-red radiation attributable

2.155 eV EMISSION SYSTEM

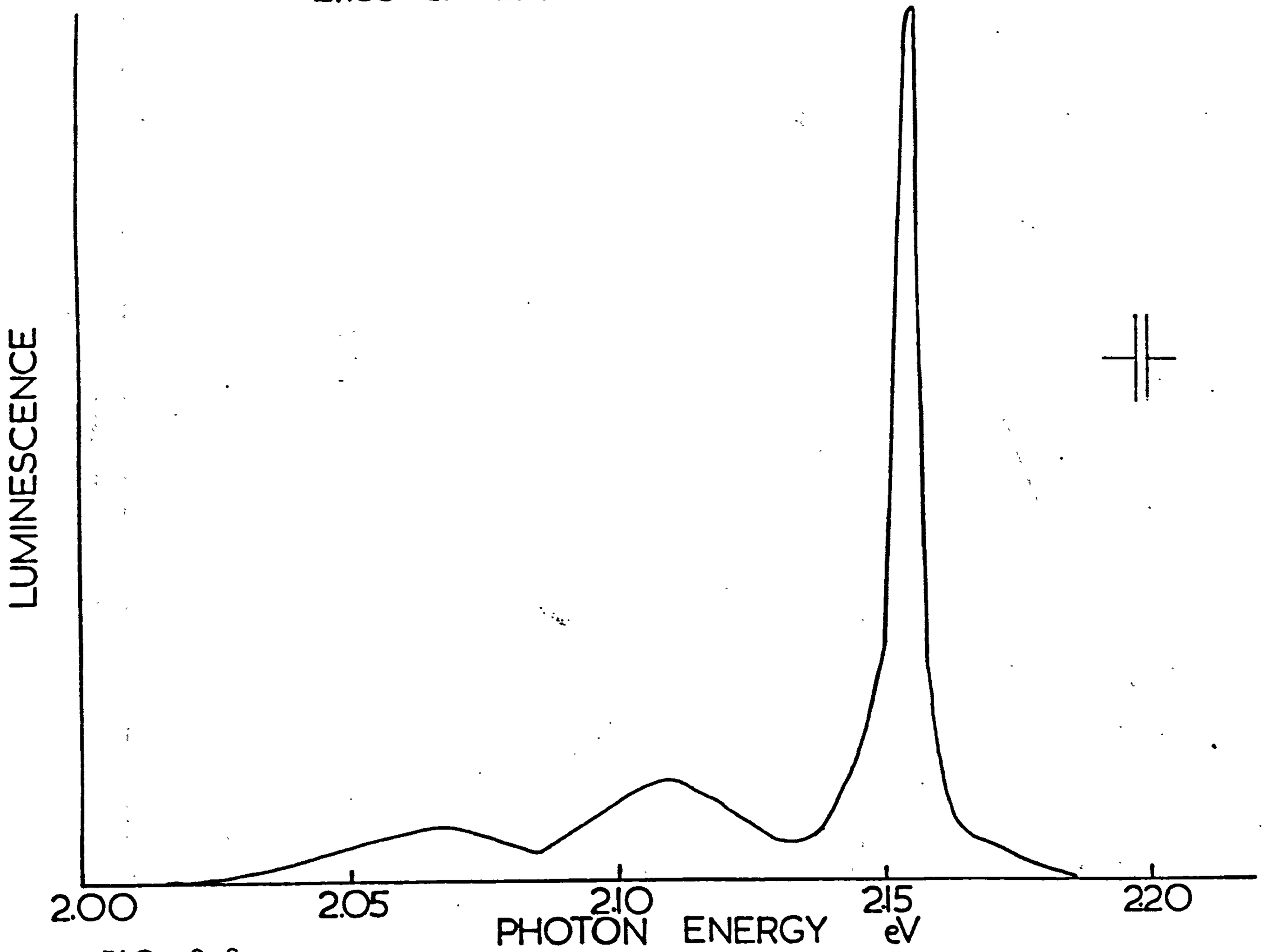


FIG. 3.8

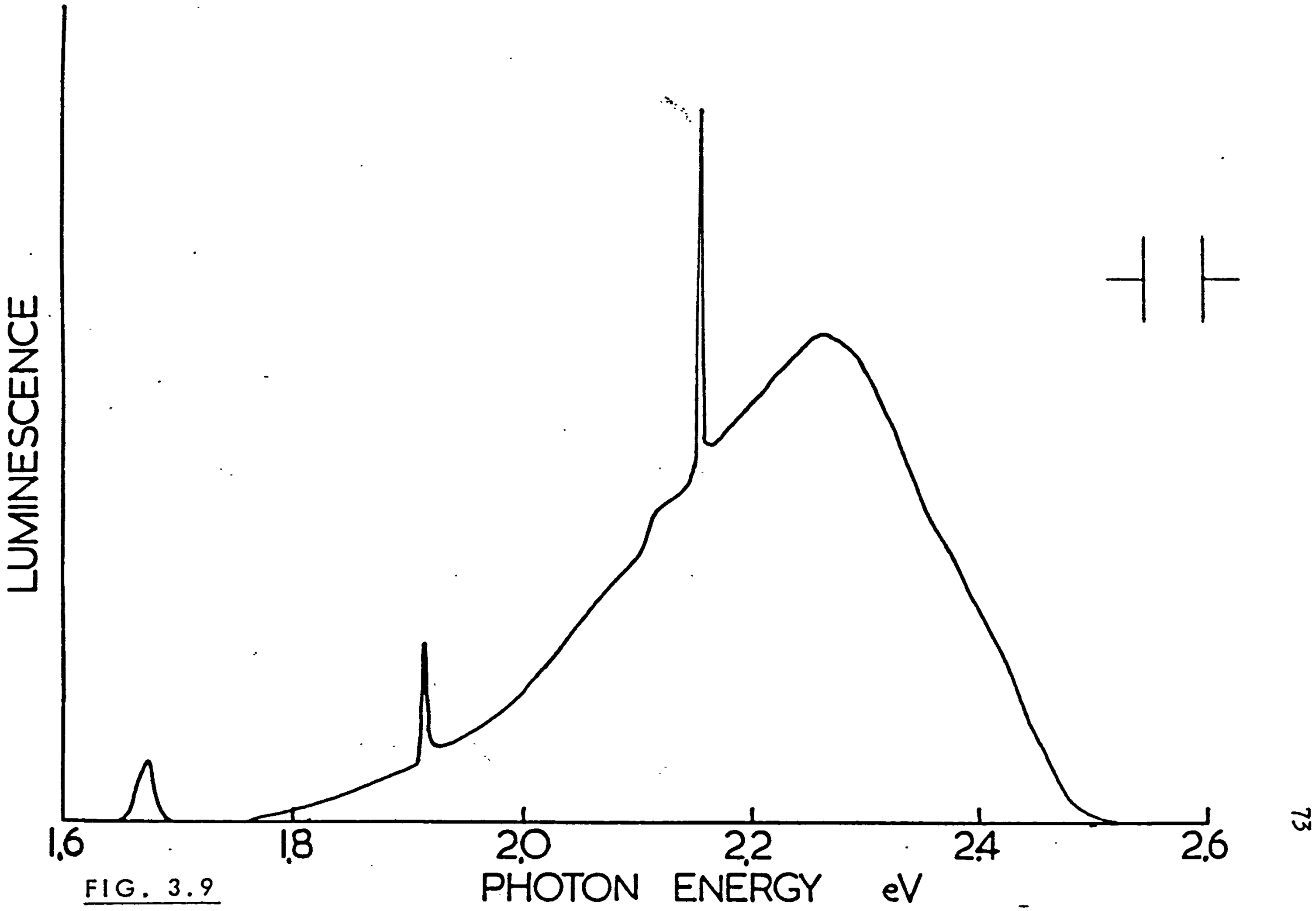
Fe B/C EMISSION
LUMINESCENCE
x 25
1.6
1.8
2.0
2.2
2.4
2.6
PHOTON ENERGY eV

FIG. 3.9

800 meV EMISSION SYSTEM

IN Fe B/C

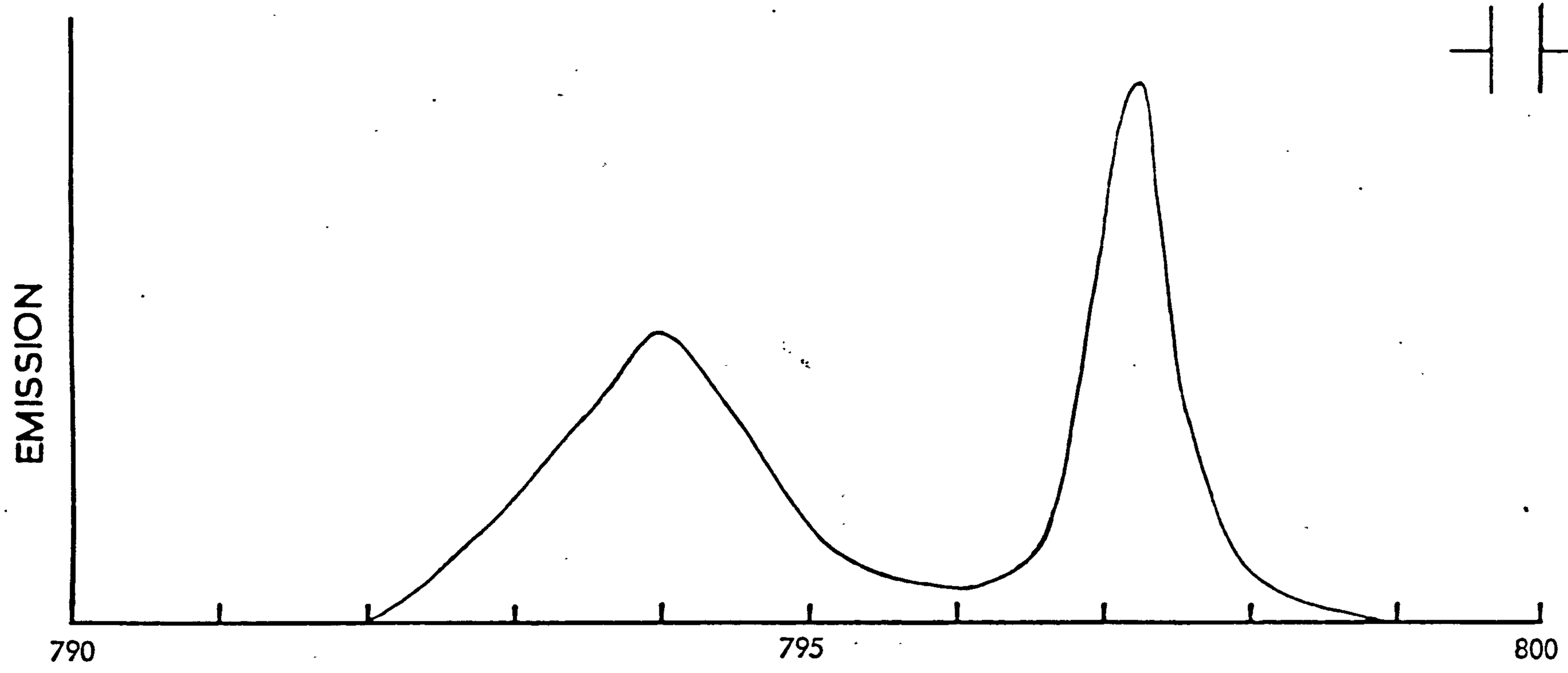


FIG. 3.10

to radiation damage yielded a previously unobserved system consisting of a doublet at photon energies of 794 meV and 797 meV as shown in fig. 3.10, recorded for specimen FeB/C at 80K. The system was detected only in those specimens which exhibited extremely intense 2.155 eV emission, and even then was exceptionally weak. It appears that the doublet arises from a transition at the same centre as the 2.155 eV system, but the low levels of infra-red emission prevented any quantitative correlation of the two systems, or of the temperature dependence of the doublet peaks. It is thus unknown whether the doublet arises from ground state splitting or from transitions involving different excited states.

Wight (1968) reported the presence of two weak emission systems in synthetic diamond after radiation damage. The systems occurred as zero phonon lines at 1.3 eV and 1.1 eV. The former had a somewhat spurious occurrence, while the latter appeared to bear a constant intensity ratio to 2.155 eV emission. Neither of these systems has been observed in the present work, even in one specimen in which Wight observed the 1.1 eV system. Whilst no comment can be made on the 1.3 eV system, it does seem that the 1.1 eV line was, in fact, the 2.155 eV system being observed in second order on the monochromator used by Wight, and consequently greatly reduced in intensity.

## Sec. 3.6. Absorption in synthetic diamonds after thermal annealing of radiation damage.

When a material is heated to sufficiently high temperatures,

it is to be expected that any impurity centres and defects therein become mobile and consequently migrate throughout the lattice until trapped at some other centre. This section deals with the products of annealing synthetic diamond at 800°C for 2 hours.

All the synthetic diamonds, having been annealed in vacuo, were found to be red in colour, the deepest coloration being observed in the diamonds of highest nitrogen content. This is similar to the effect produced when annealing natural type Ib diamond. The coloration is produced by the strong phonon band associated with the 1.945 eV zero phonon absorption line (du Preez, 1965). The absorption found in sample 71/134D is shown in fig. 3.11. The 1.945 eV zero phonon line is seen to couple most strongly with 60 meV phonons and the system was proposed by du Preez to be produced by the migration of GRI vacancies to the isolated nitrogen impurities, a hypothesis to be discussed in chapter 5.

The absorption of the above phonon band is distorted by the presence of the 2.083 eV (595.5 nm) zero phonon line. It was reported in section 3.4 that such a line was seen in synthetic diamond of low nitrogen content before annealing, and in such specimens this absorption feature was enhanced by typically 30% during annealing. In addition, the line was produced in specimens of higher nitrogen content in which it had not been detected before annealing. The 2.083 eV line has been seen in natural type Ib diamond by Davies (1972) and during the present work. An unpublished attempt by Davies to determine its symmetry properties

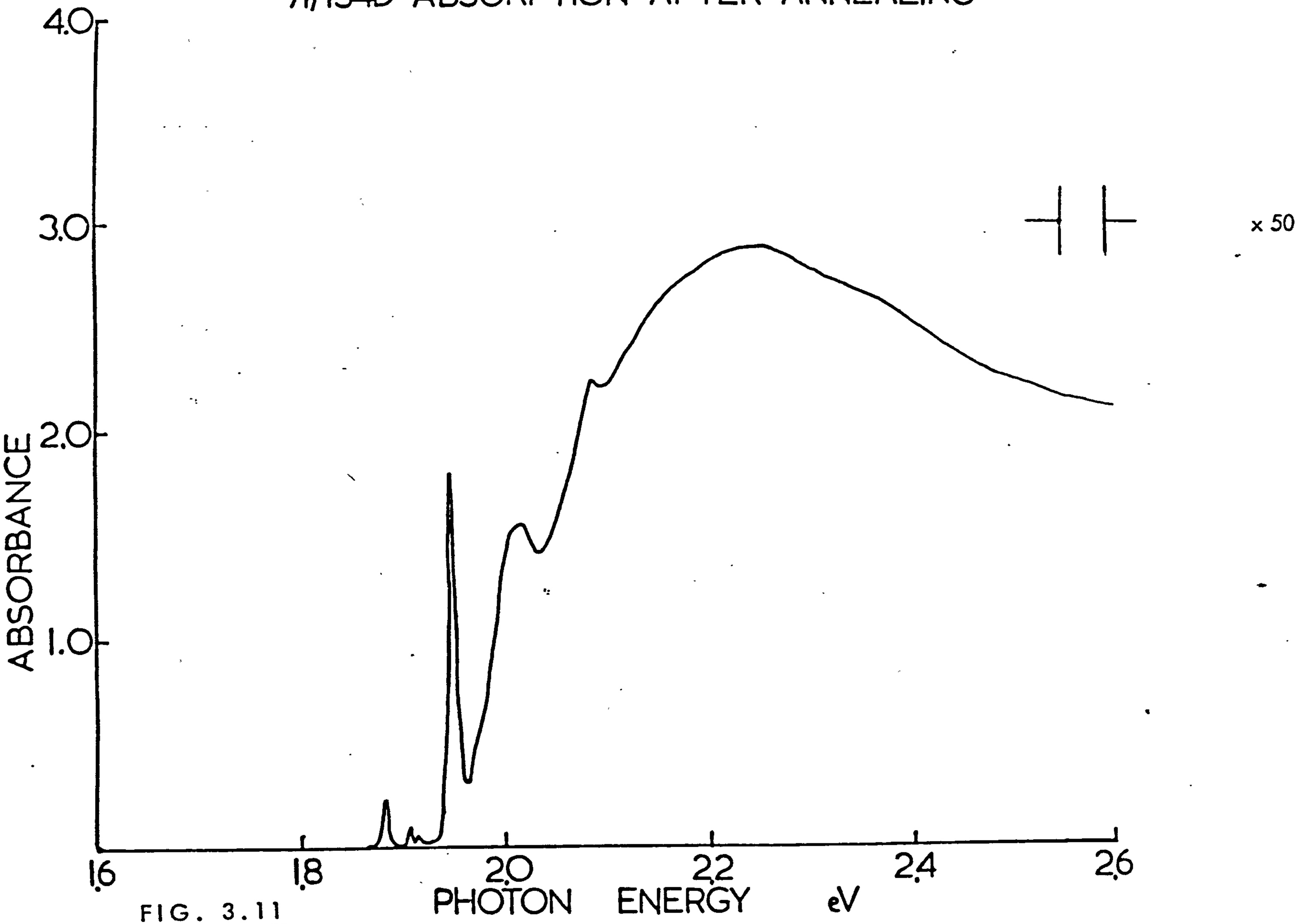
71/134D ABSORPTION AFTER ANNEALING
4.0
3.0
2.0
1.0
ABSORBANCE
x 50
1.6
1.8
2.0
2.2
2.4
2.6
PHOTON ENERGY eV

FIG. 3.11

as a result of stress measurements was unsuccessful because of the apparent reorientation of the centre involved upon application of such stress.

In all diamonds, both GRI and NDI had annealed out after 2 hours at 800°C, as also had the 2.010 eV peak reported in sec. 3.4. Fig. 3.11 does show, however, the continued presence of the singlet and doublet lines around 1.9 eV designated as A and A' in fig. 3.4, although features B and C, if still present, are masked by intense 1.945 eV absorption. Annealing did not however, enhance features A and A' or produce such lines in diamonds where they had not previously been observed. It thus seems that the centre involved is one of low mobility and associated with nitrogen in the lattice.

Annealing for rather longer periods of time than 2 hours produced absorption at 2.155 eV in a number of specimens of low nitrogen content. This is interpreted as the absorption analogue of the 2.155 eV cathodoluminescence system, which has also been observed in luminescence excitation (Davies 1976). The emission at 2.155 eV would thus not appear to be an inter-excited state transition, which further suggests that the splitting of the emission doublet around 0.795 meV is not caused by ground state splitting, if indeed the systems are related.

## Sec. 3.7 Cathodoluminescence in synthetic diamond after thermal annealing of radiation damage.

After thermal annealing, only one nitrogen dependent emission system was observed, namely that consisting of two singlet lines and a doublet around 2.55 eV which has been reported in sec. 3.5.

The system was generally found to be of comparable intensity before and after annealing. All specimens showed increased emission at 2.155 eV and at 0.8 eV whilst the 3.188 eV zero phonon line and associated phonon structure were seen to be of similar intensity as before annealing, further showing the distinction between this system and the NDI absorption system.

## Sec. 3.8 Conclusions.

The existence has been verified of a number of previously documented optical features in synthetic diamond, produced by radiation damage. Tables I and II list such features, along with previously unobserved systems according to the nitrogen content of such diamonds. Isolated nitrogen is seemingly responsible for absorption features at 3.149 eV (NDI), 2.367 eV, 1.979 eV, 1.9 eV and 1.945 eV and for emission around 2.6 eV. Hitherto unobserved absorption has been detected corresponding to 2.155 eV emission and an infra-red emission system has been observed at $\sim$ 795 meV which correlates qualitatively with 2.155 eV emission.

Table I

Absorption features due to radiation damage in synthetic diamond.

| Zero phonon line(eV | Impurity Content > 50n.p.m. | | Impurity Content < 50p.p.m. | |
|---|---|---|---|---|
| | Before Thermal Anneal | After Thermal Anneal | Before Thermal Anneal | After Thermal Anneal |
| 3.149(NDI) | Strong | No | Weak | No |
| 2.535 | Weak | No | Weak | No |
| 2.443 | Weak | No | Weak | No |
| 2.367 | Strong | No | No | No |
| 2.155 | No | No | No | Weak |
| 2.083 | No | Weak | Weak | Weak |
| 2.010 | No | No | Weak(infrequent) | No |
| 1.979 | Weak | No | No | No |
| 1.943 | Weak(infrequent) | No | No | No |
| 1.945 | No | Strong | No | Quite strong |
| 1.883, 1.906, 1.913 | Weak | Weak | No | No |
| 1.673(GRI) | Weak | No | Weak | No |

Table II

Cathodoluminescence features due to radiation damage in synthetic diamonds.

| Zero phonon line(eV) | Impurity Content > 50p.p.m. | | Impurity Content < 50p.p.m. | |
|---|---|---|---|---|
| | Before Thermal Anneal | After Thermal Anneal | Before Thermal Anneal | After Thermal Anneal |
| 3.188 | Strong | Strong | Strong | Strong |
| 2.595<br>2.562<br>2.538<br>2.533 | Strong | Strong | No | No |
| 2.465(H3) | Weak | Weak | No | No |
| 2.155 | Strong(after electron beam anneal) | Strong | Strong(after electron beam anneal) | Strong |
| 1.912 | No | No | Weak(infrequent) | No |
| 1.673(GRI) | No | No | Weak(infrequent) | No |
| 0.8 | Weak | Weak | Weak | Weak |

## Chapter 3

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| | | | | |
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# Chapter 4

## The 2.367 eV absorption system in synthetic and natural type Ib diamond.

### Sec. 4.1 Introduction.

Chapter 3 has reported the observation of several new optical absorption and emission systems in synthetic diamonds as a result of radiation damage by 2 MeV electrons. This chapter deals specifically with one such absorption system which has a zero phonon transition of energy 2.367 eV at 80K. It has been seen that this system is detected in synthetic diamonds of relatively high nitrogen content. Since such diamonds are considered to have only isolated nitrogen atoms present in sufficient quantities to produce strong absorption systems, it is probable that the transition in question occurs at a centre comprising a radiation damage product and one or more isolated substitutional nitrogen atoms.

The zero phonon transition at 2.367 eV has also been detected in absorption, during the course of the present work, in a natural type Ib diamond after radiation damage. No corresponding absorption has been observed in irradiated type Ia diamonds, which further points to the dependence of the system upon isolated nitrogen in the lattice.

Sec. 4.2 Phonon assisted transitions associated with the 2.367 eV system.

Absorption by the system in question is shown in fig. 4.1, as recorded for a natural type Ib diamond at 80K. In this spectral region, natural type Ib diamond is seen to show several zero phonon transitions associated with radiation damage. These transitions will be discussed in order to ascertain those spectral features attributable to the 2.367 eV system. To aid comparison between natural and synthetic diamond, fig. 4.1 adopts the same nomenclature for the various spectral features as was used in fig. 3.4 of the previous chapter. The 2.367 eV zero phonon line is recognised as feature D, whilst lines E and F at 2.442 eV and 2.535 eV respectively, are seen to be present with a different intensity ratio from that observed in synthetic Ib diamond, as reported in section 3.4.

Zero phonon line G at 2.462 eV which has a low energy tail, and the feature at 2.484 eV, have no counterpart in synthetic diamonds at low irradiation levels, but line G has been observed in all other types of diamond, particularly strongly after irradiation by very high energy electrons (Davies 1974). The line is now designated as the 3H feature, and has been shown by Davies to exhibit weak phonon coupling, selecting 66 meV phonons particularly. The first phonon replica of G would thus predominantly fall under feature F of fig. 4.1, accounting for the asymmetry of this latter zero phonon line. Davies has shown the symmetric line G to be produced in proportion to the GRI system in natural diamonds, and also that it readily anneals out, at variance with the GRI system. In addition, Davies has shown that the zero phonon line G is enhanced by high nitrogen content, despite nitrogen not being essential for its formation.

ABSORPTION IN NATURAL Ib DIAMOND

AFTER RADIATION DAMAGE

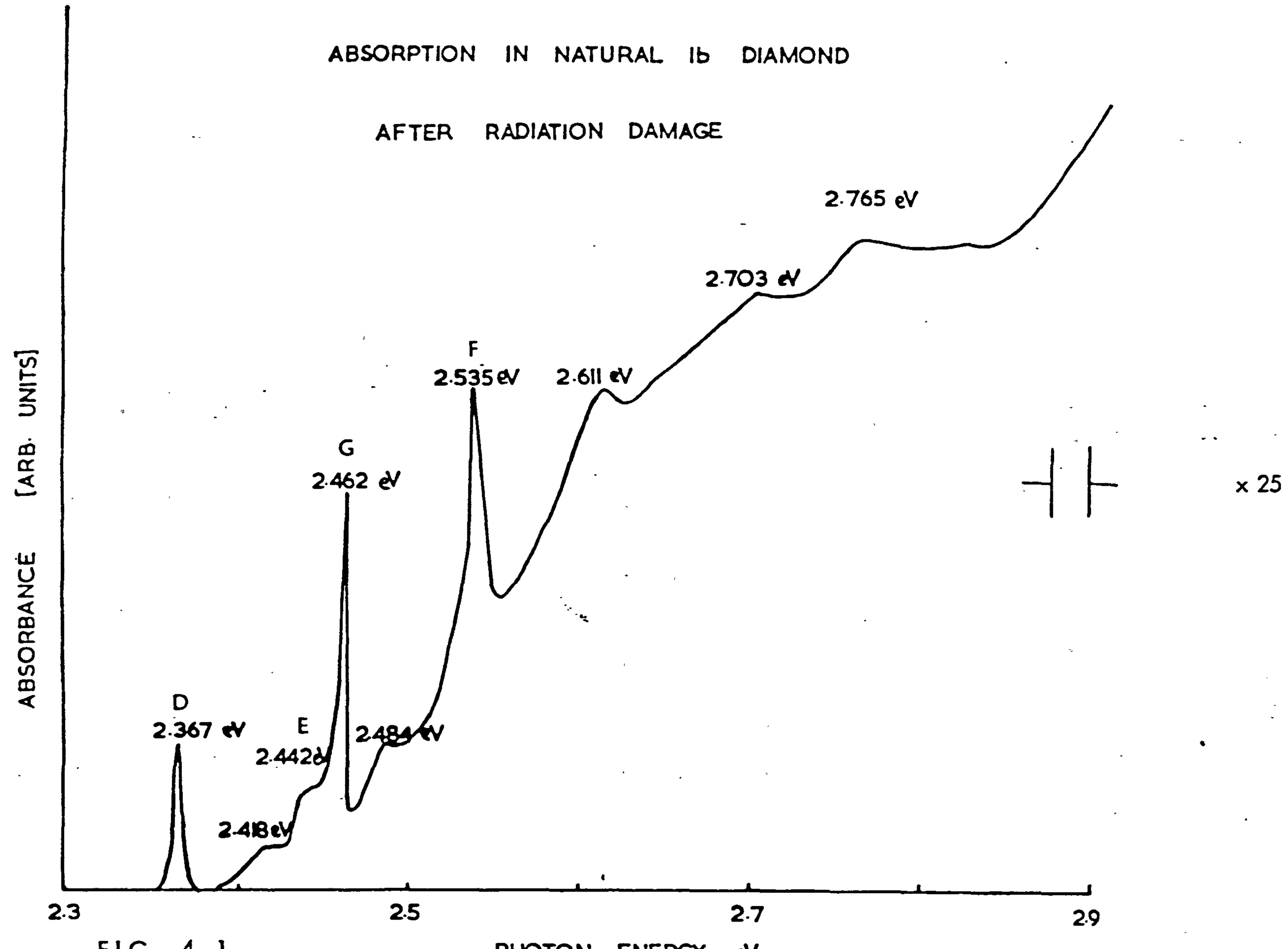


FIG. 4.1

As a consequence of the above considerations it is seen that only the broad feature at 2.418 eV has not been identified. Since no zero phonon line has been observed within the range 165 meV (Raman phonon energy) below D at 2.367 eV, it is thus assumed that the absorption around 2.418 eV is in fact the first phonon replica of feature D , suggesting that the transition exhibits only weak phonon coupling, predominantly of energy about 51 meV.

Isolation of the 2.367 eV peak and its possible first phonon replica was found to be impracticable since thermal annealing at 300°C caused rapid reduction of the system whilst the 2.462 eV peak was not noticeably affected by temperatures below 500°C. In addition, synthetic diamond of sufficient nitrogen content to produce appreciable 2.367 eV absorption have a sharply rising background absorption in this region, thus preventing positive identification of the phonon replicas of the 2.367 eV peak. Complete identification of the 2.367 eV system and its phonon assisted transitions is thus impracticable.

## Sec. 4.3. Optical bleaching of the 2.367 eV line.

Radiation damage centres in diamond are known to be photochromic i.e. the absorption associated with such centres can be altered by light of certain energies falling upon the diamond. Such changes can usually be reversed by warming the diamond to a suitable temperature, dependent upon the centre involved. Dyer and du Preez (1965) showed such effects in the GRI system, for which periods of several hours at 500°C were required to reverse

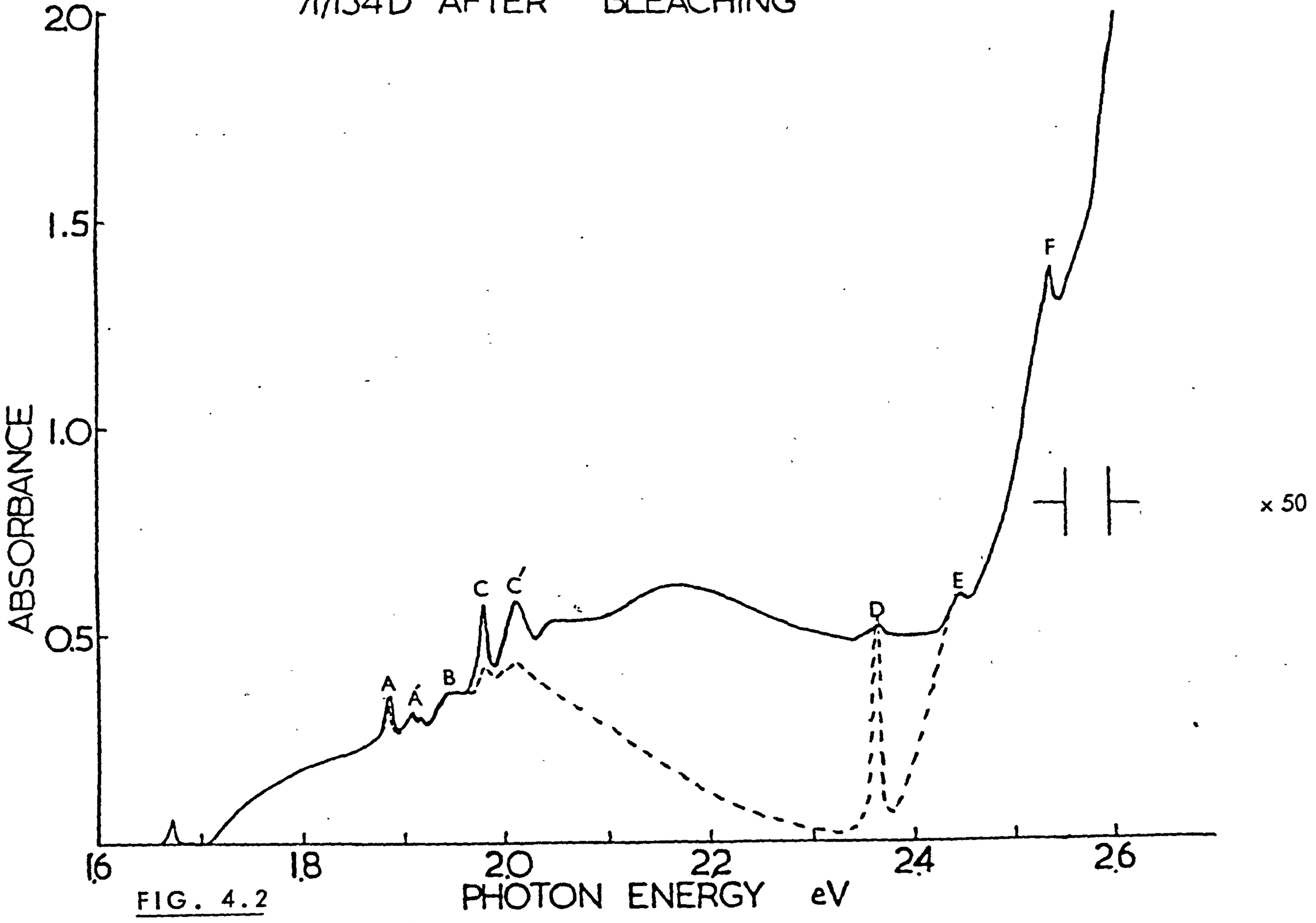
71/134D AFTER BLEACHING
20
1.5
1.0
0.5
ABSORBANCE
A
Á
B
C
C'
D
E
F
× 50
1.6
1.8
2.0
2.2
2.4
2.6
PHOTON ENERGY eV

FIG. 4.2

the effects of shining unfiltered light from a mercury lamp on the diamond. The phenomenon can be attributed, in the simplest case, to charge transfer between two centres being stimulated by light or heat. The optical absorption of one system thus grows while another decreases.

During the present work it was seen that repetitive measurements of the absorption of all diamonds exhibiting the 2.367 eV system gave changing results for absorption in the photon energy range 2.0 eV to 2.4 eV. Fig. 3.4 showed absorption in synthetic diamond 71/134D at the start of an experimental run at a temperature of 80K, in which the light source was 100W quartz-iodine lamp. With no change in experimental conditions, the absorption produced by the specimen after 3 hours of illumination, was as shown in fig. 4.2 upon which the results of fig. 3.4 are superimposed for comparison. It is seen that the background absorption in the region 2.0 eV to 2.4 eV is considerably increased to the detriment of the absorption at 2.367 eV. In addition, features A, A', and B are increased in intensity by about 5%, whilst features C and C' are dramatically increased in intensity. Lines E and F , of higherenergy than 2.367 eV are, however, unaffected by the decrease of 2.367 eV absorption.

The spectral changes reported above were observed in all synthetic diamonds exhibiting 2.367 eV absorption, and in the single natural type Ib diamond available for examination. At a temperature of 80K, the 2.367 eV system could be bleached to extinction, after which time no further changes in the absorption

between 2.0 eV and 2.4 eV could be detected. After allowing the diamond to return to room temperature, and then recooling, it was found that the 2.367 eV line always returned to its original intensity, and bleaching could be carried out once more. In addition, a partially bleached 2.367 eV line, upon being left in the dark at 80K, was found to be restored to its original state after several hours.

Since the photochromic effects associated with the 2.367 eV line are easily reversed at room temperature, without accompanying annealing of the system as in the case of GRI centres, the 2.367 eV line was considered suitable for a further investigation into such phenomena.

In order to ascertain the method by which charge is released from 2.367 eV centres, the rate of bleaching of the line was studied using a variety of optical filters between light source and specimen. It was found that the rate of bleaching of the line in a given diamond was practically unaffected by use of a filter which did not transmit light of energy below about 2.3 eV in appreciable quantities. Consequently, it is suggested that the centre is ionised by radiation of energy 2.367 eV, and the charge thereby released is preferentially trapped at centres of lower energy.

In view of the thermal repopulation of 2.367 eV centres, which is more rapid at higher temperatures, it seems reasonable to suggest that if charge is thermally released from traps of energy $E$, then the repopulation will depend upon temperature according to the relationship :-

The rate of repopulation is proportional to $C \exp^{-E/kT}$

where $C$ is a constant, k is Boltzmann's constant and $T$ the absolute temperature. If several traps are involved, each of different energy, then the repopulation might be expected to be proportional to a summation of such terms as the above

i.e. rate of repopulation is proportional to $\sum_I C_I \exp^{-E_i/kT}$

If we let the absorption of the 2.367 eV line at any instant be $A$ , $A_0$ being its value before commencement of bleaching, then we can assume that the rate of repopulation of 2.367 eV centres is proportional to the charge liberated, by bleaching, from 2.367 eV centres i.e. proportional to $(A_0 - A)$. Thus we can represent the rate of repopulation of 2.367 eV centres by

$(A_0 - A)\sum_i C_i \exp^{-E_i/kT}$

The rate of depopulation of 2.367 eV centres by photons can be assumed to be proportional to the number of unionised 2.367 eV centres i.e. depopulation varies as $\propto A$ where $\propto$ is a constant dependent upon the intensity of light falling on the diamond.

Combining the above considerations we can thus derive a possible equation representing the rate of reduction of the 2.367 eV absorption strength

$$\frac{dA}{dt} = -\propto A + (A_o - A)\sum_i C_i \exp^{-E_i/kT} \qquad \text{eq. 4.1}$$

The solution of eq. 4.1 can be written as

$$A = A_0\left(\frac{\alpha}{\alpha+\beta}\right)\exp^{-(\alpha+\beta)t} + \frac{\beta A_0}{\alpha+\beta} \qquad \text{eq. 4.2}$$

where $\beta = \sum_i C_i \exp^{-E_i/kT}$

The suitability of equation 4.1 has been tested by measuring the rate of optical bleaching of the 2.367 eV zero phonon line over a range of temperatures. Since constant $\alpha$ of equations 4.1 and 4.2 is dependent upon the density of photons falling on the specimen it was necessary to ensure that the diamond received a constantradiant intensity at all temperatures. This was ensured as follows.

A filter was placed between light source and specimen, such that only radiation of energy below 2.3 eV fell upon the specimen, thus producing no bleaching of the 2.367 eV line. The specimen and source were then aligned so that a constant signal was produced by the photomultiplier detector at a photon energy of 1.8 eV, absorption by the diamonds at this energy having been found to be independent of specimen temperature. Thus, a constant radiant intensity was focussed onto the diamond at all temperatures.

The typical results of bleaching at various temperatures are shown in fig. 4.3, as recorded for synthetic diamond 71/134D. The behaviour predicted by equation 4.2 is followed quite well, particularly at higher temperatures. Further examination of the curves does not, however, yield a consistent set of values for $C_i$

OPTICAL BLEACHING OF 2.367eV LINE
IN SYNTHETIC DIAMOND 71/134/D.



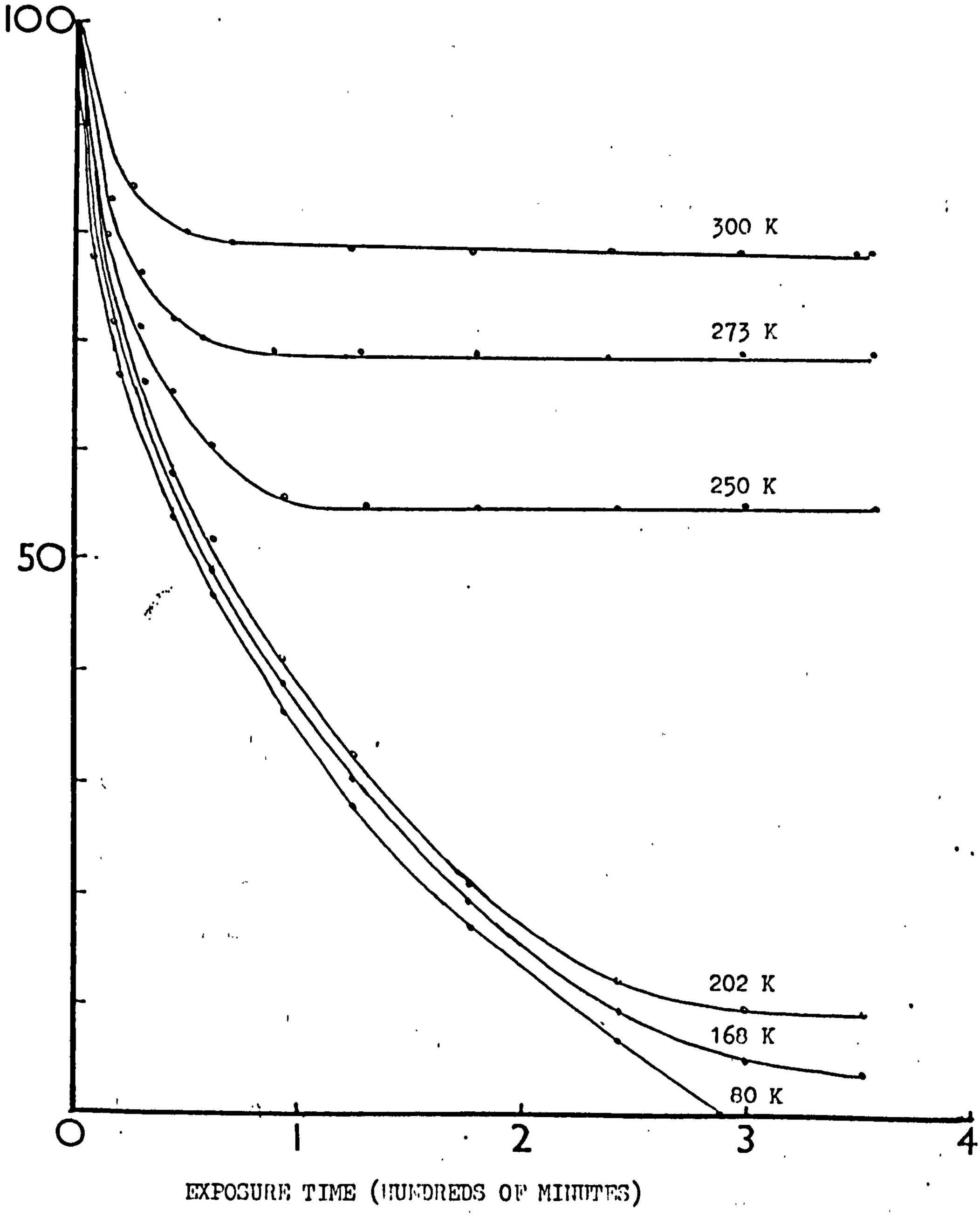


FIG. 4.3

and $E_i$ when two separate centres are considered to be responsible for trapping of charge released from 2.367 eV centres. It thus seems likely that more than two centres are involved, which is not surprising in view of the dramatic increase in background absorption during bleaching, or else the model proposed is too simple. (See also Appendix at end of Thesis)

Particularly interesting is the behaviour of the 2.367 eV line below about 250K, when the rate of bleaching is very temperature sensitive. In addition, below 150K, the bleaching deviates from it exponential behaviour, suggesting that the rate of charge release from 2.367 eV centres is not dependent upon the number of unionised 2.367 eV centres. Indeed below about 150K the 2.367 eV line could be completely extinguished in a finite time. This was found to be particularly true at extremely low temperatures, the line disappearing after 2 minutes at 5K. Since the rate of bleaching was so rapid at such temperatures further details of the shape of the relevant bleaching curves were not obtainable.

Holding the specimen at 5K in the dark produced no observable repopulation of 2.367 eV centres, and so a "hopping" of charge between centres, as part of the repopulation process, seems unlikely. A thermal repopulation of 2.367 eV centres is thus proposed as the means of reversing optical bleaching of the system, but it is by no means clear what is the nature of the centres trapping charge liberated from 2.367 eV centres by photons.

## Sec. 4.4. Temperature dependence of the 2.367 eV system .

This section briefly outlines the theory relevant to a description of the temperature dependence of a vibronic system such as that having a zero phonon line at 2.367 eV. Before a detailed analysis of a vibronic system can be attempted, it is first necessary to ascertain the general shape of a zero phonon line, since such shape is a result of the interaction of the electronic transition with the phonons present at a finite temperature. As seen in fig. 4.1, the zero phonon line in question has a full width at half height of typically 4 meV at 80K. This line width is only marginally reduced at lower temperatures, the residual line width at 0K being the result of strain within the crystal. Such a residual effect leads to changes of line shape from that observed when no strain perturbations affect the transitions involved.

It has been shown by Maradudin (1966) that the shape of a zero phonon line at finite temperature, as determined by phonon interactions above, obeys a Lorentzian distribution, i.e.

$$I(\nu) = \frac{\alpha}{\beta + (\nu - \nu_0)^2} \qquad \text{eq. 4.3}$$

where $\alpha$ , $\beta$ , $\nu_0$ determine peak height, width, and position of the zero phonon line. Consequently, the shape of a zero phonon line in a strained lattice is a convolution of equation 4.3 and the low temperature line shape produced by strain effects alone. Such

a convolution has been shown by Davies (1969) to lead to a line shape of the general form

$$I(\nu) = \frac{A}{[B + (\nu - \nu_0)^2]^2} \qquad \text{eq. 4.4}$$

This so-called bi-Lorentzian shape has been found by Davies (1970) to describe a number of zero phonon line shapes in diamond, both in absorption and emission e.g. NDI absorption, 3.188 eV emission, H3 emission and absorption.

The effects of phonon broadening, as a function of temperature, upon the peak position, width, and integrated absorption of a zero phonon line have been considered by Maradudin (1966), Imbusch et al (1964), and McCumber (1964). A résumé of the results of these authors is now given. The phonon coupling to the electronic configuration of the defect centre is described in terms of $\rho(\omega)$, the density of states at a phonon frequency $\omega$. The three main parameters describing the zero phonon line at any temperature are the shift, $\Delta(T)$, of the peak position of the line from its OK value, the full width at half height of the line, $2\Gamma(T)$, and the ratio of the zero phonon line intensity $I_0(T)$ to the total intensity of the whole system, $I(T)$. The parameters are defined by Maradudin (1966) as follows:-

$$\Delta(T) = \alpha \int_0^{\omega_D} \rho(\omega)\, n(\omega)\, d\omega \qquad \text{eq. 4.5}$$

$$\Gamma(T) = a_2 \int_0^{\omega_D} [\rho(\omega)]^2 n(\omega)(n(\omega)+1)\, d\omega \qquad \text{eq. 4.6}$$

$$\frac{I_o(T)}{I(T)} = \exp^{-M} \qquad \text{eq. 4.7}$$

$$\text{where } M = a_3 \int_0^{\omega_D} \frac{\rho(\omega)}{\omega^2}(1 + 2\, n(\omega))\, d\omega \qquad \text{eq. 4.8}$$

$a_1$, $a_2$, $a_3$, are constants, and $n(\omega)$ is the probability of a phonon state being occupied at temperature T i.e.

$$n(\omega) = [\exp(\hbar\omega/kT) - 1]^{-1}$$

$\omega_D$ is the Debye cut off frequency i.e. the highest frequency at which the lattice around the defect can vibrate.

In the case of totally symmetric electron-phonon coupling, the density of phonon states varies as $\omega^3$, whereupon eq. 4.7 reduces to

$$\frac{I_o(T)}{I(T)} = \exp -S(1 + 6.58T^2/\theta_D^2) \qquad \text{eq. 4.9}$$

S is the Huang-Rhys factor, and $\theta_D$ the Debye cut off temperature, defined by $\theta_D = \frac{\hbar\omega_D}{k}$

Equation 4.9 is strictly valid for temperatures well below $\theta_D$, with a $\omega^3$ phonon distribution. In practice it has been found to hold in much more complicated cases than that of symmetric coupling, e.g. $F^+$ centre in Ca O (Escribe and Hughes 1971).

The fraction of the whole absorption or emission system taken up in the zero phonon line is strictly only calculable by observing the entire system involved. However, as shown by Davies (1969), the integrated absorption of a typical vibronic system in diamond is independent of temperature, to within experimental error, and, consequently, only the temperature dependence of the zero phonon line strength need be investigated.

## Sec. 4.5 Experimental.

As a consequence of the optical bleaching of the 2.367 eV line, it will be appreciated that it is not practicable to perform a continuous series of measurements upon the zero phonon line over a range of temperatures. This difficulty was circumvented in the following manner. After a measurement at a given temperature, the specimen temperature was adjusted to that required for the next measurement, and the specimen repositioned, if necessary in the light beam. The specimen was then warmed to room temperature so as to repopulate the 2.367 eV centres, and then recooled to the required temperature. In this manner it was found that reproducible results were obtainable at temperatures above about 40K. Below this temperature, the system was found to bleach too rapidly during measurement of the zero phonon line, for any reliability to be placed upon values of absorption coefficients, line position, or line width.

## Sec. 4.6 Results and discussions.

The typical shape of the 2.367 eV zero phonon line is shown in fig. 4.4, as recorded for a natural type Ib diamond at 77K. The computed best fit to the experimental points, representing Lorentzian and bi-Lorentzian line shapes are also shown, and it can be seen that a very good fit to the data is provided by the bi-Lorentzian distribution. Fig. 4.5 presents the same analysis for a specimen temperature of 295K, and again it is seen that a bi-Lorentzian line shape produces the best fit to the experimental points. The bi-Lorentzian line shape will thus be used to describe the line in question at temperatures up to 300K.

It has been seen in section 4.2 that isolation of the 2.367 eV system from neighbouring absorption systems was not found to be possible, and that, consequently, the density of phonon states, $\rho(\omega)$, associated with the centre involved could not be experimentally determined. A Debye distribution has thus been assumed in the analysis of the system. Knowledge of the low temperature limits of zero phonon line absorption, width, and peak position, and the bi-Lorentzian line shape have been used as data for a computer program due to Davies (1969), assuming a Debye phonon distribution. A series of trial values of Debye cut off frequency $\omega_D$ has been used to determine the best theoretical fits to the above parameters at temperatures up to 300K.

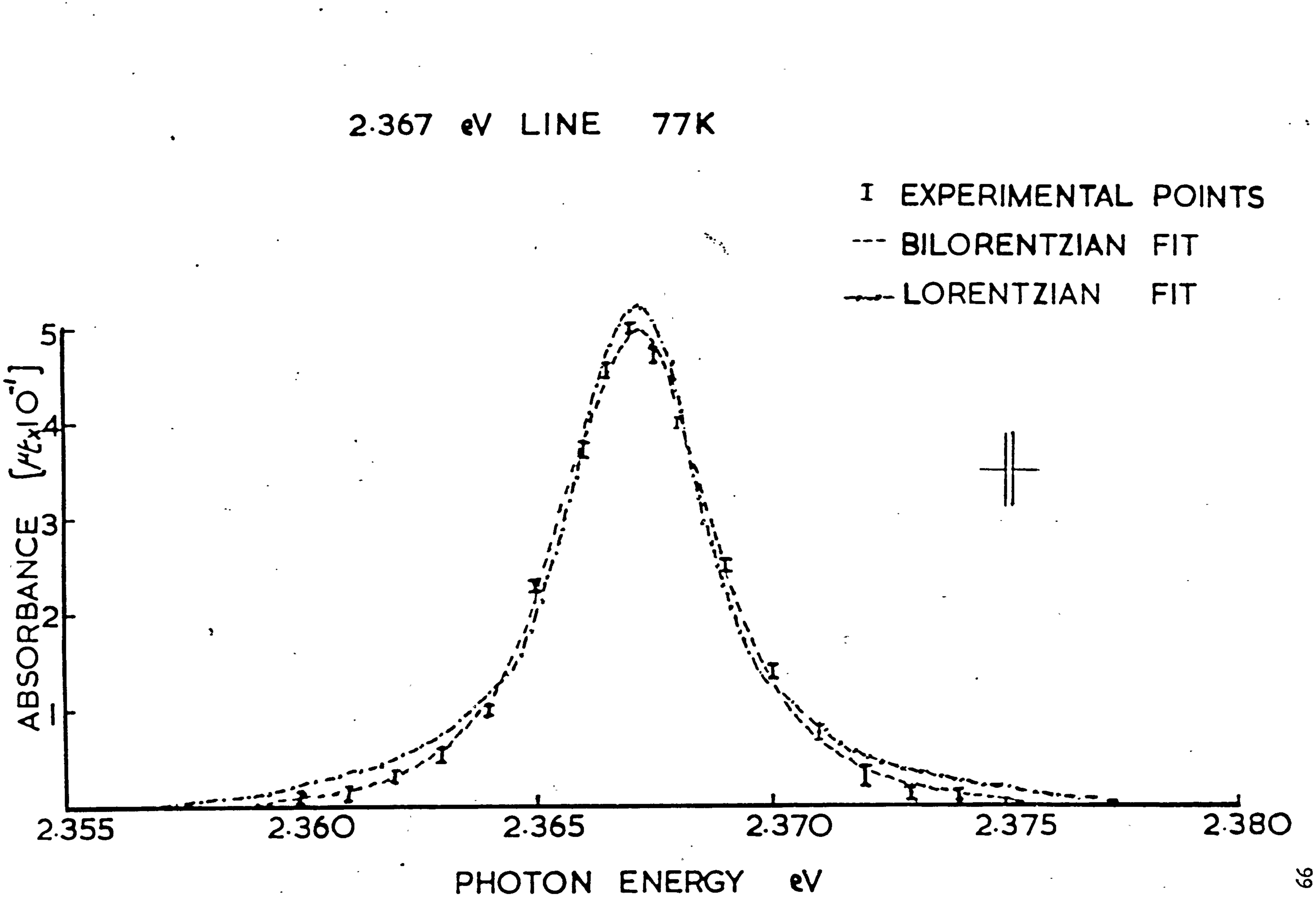
2·367 eV LINE 77K
I EXPERIMENTAL POINTS
--- BILORENTZIAN FIT
—·— LORENTZIAN FIT
ABSORBANCE [μt x 10⁻¹]
5
4
3
2
1
2·355
2·360
2·365
2·370
2·375
2·380
PHOTON ENERGY eV

FIG. 4.4

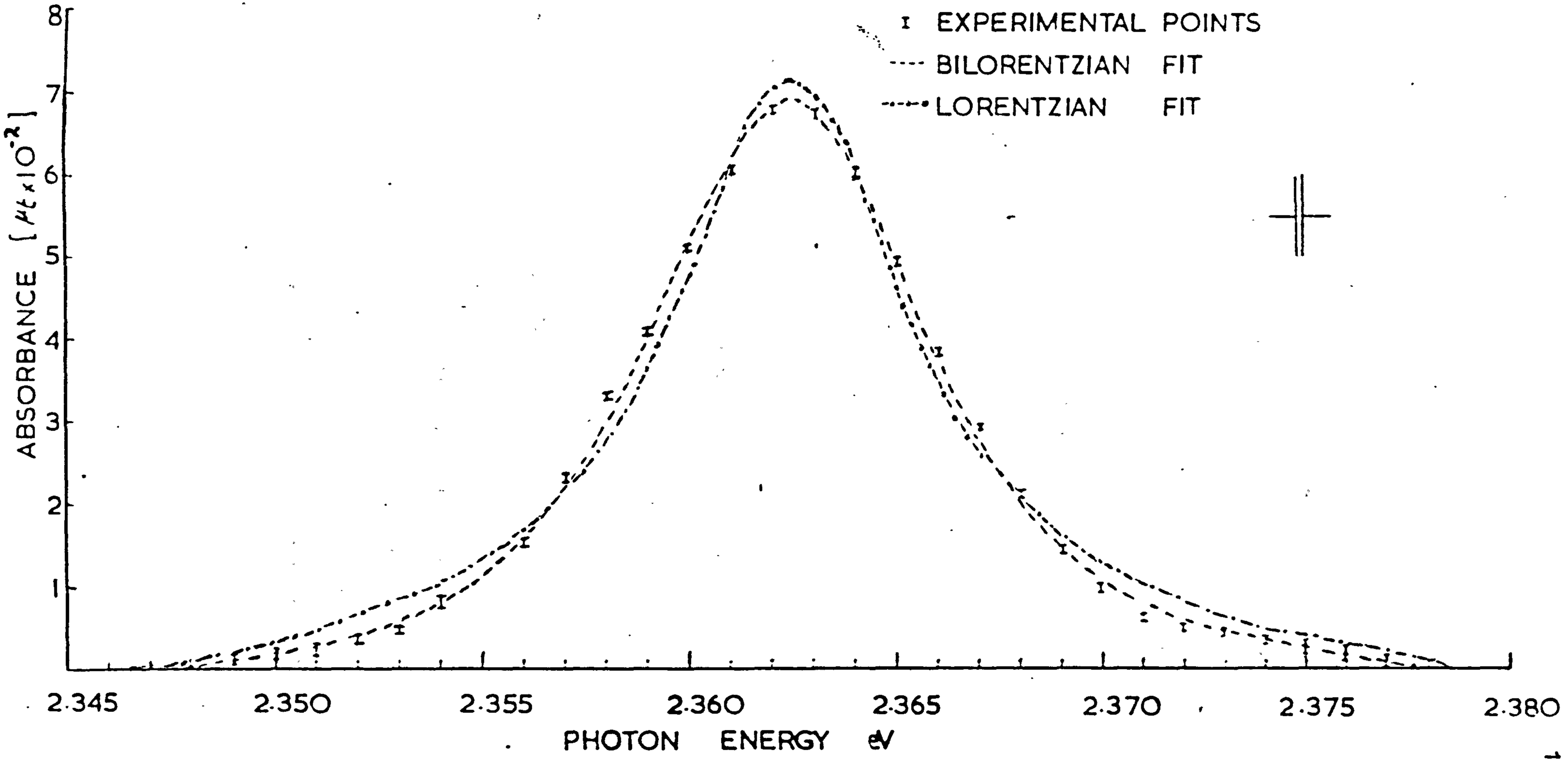
2.367 eV PEAK 295 K
EXPERIMENTAL POINTS
BILORENTZIAN FIT
LORENTZIAN FIT
ABSORBANCE [μℓ×10⁻²]
8
7
6
5
4
3
2
1
2.345
2.350
2.355
2.360
2.365
2.370
2.375
2.380
PHOTON ENERGY eV

FIG. 4.5

Fig. 4.6 shows the temperature variation of the integrated absorption of the zero phonon line, along with the best fit to the data, the latter provided by a Debye phonon distribution with cut off at $\hbar\omega_D = 65$ meV .The form of the variation is typical of vibronic systems in general, although the absorption falls away from its OK value rather more rapidly than is usually found to be the case in diamond. Equation 4.9 predicts that absorption at the zero phonon energy assymptotically approaches zero as the specimen temperature rises. Such a trend is exhibited by the present system.

In Fig. 4.7, the natural logarithm of the zero phonon line integrated absorption is plotted as a function of the square of absolute temperature. The linearity predicted by eq. 4.9 is seen to hold extremely well. The gradient of the line obtained yields a value of $2.62 \times 10^{-6}\ K^{-2}$ for the quantity $\frac{S}{\theta_D^2}$ . This falls within the range $10^{-6}\ K^{-2}$ to $2.7 \times 10^{-6}\ K^{-2}$ observed for other vibronic systems in diamond (Davies 1974).

The temperature dependence of the peak position of the zero phonon line is seen in fig. 4.8, along with the computed best fit to the experimental data, which is again derived from a Debye cut off at 65 meV. The linearity of the variation of peak position with temperature, at high temperatures, which is seen in fig. 4.8 is predicted by the theory of Maradudin (1966).

Fig. 4.9 shows the variation of line width with temperature. The theoretical fit to the data provided by a Debye cut off at

# TEMPERATURE DEPENDANCE OF 2.367 eV LINE IN 71/134/D

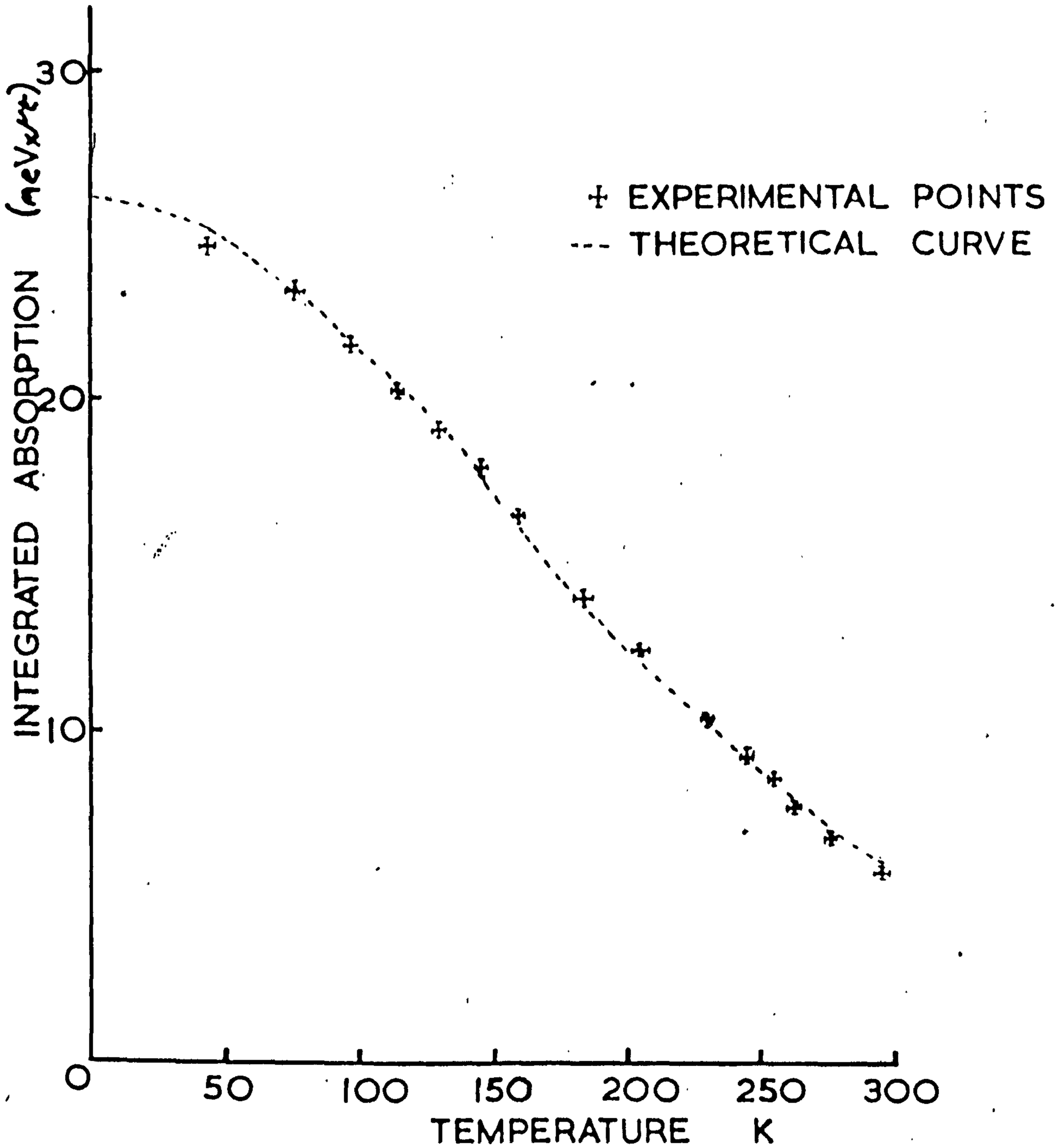


FIG. 4.6

TEMPERATURE DEPENDANCE
OF 2.367 eV LINE
IN 71/134/D

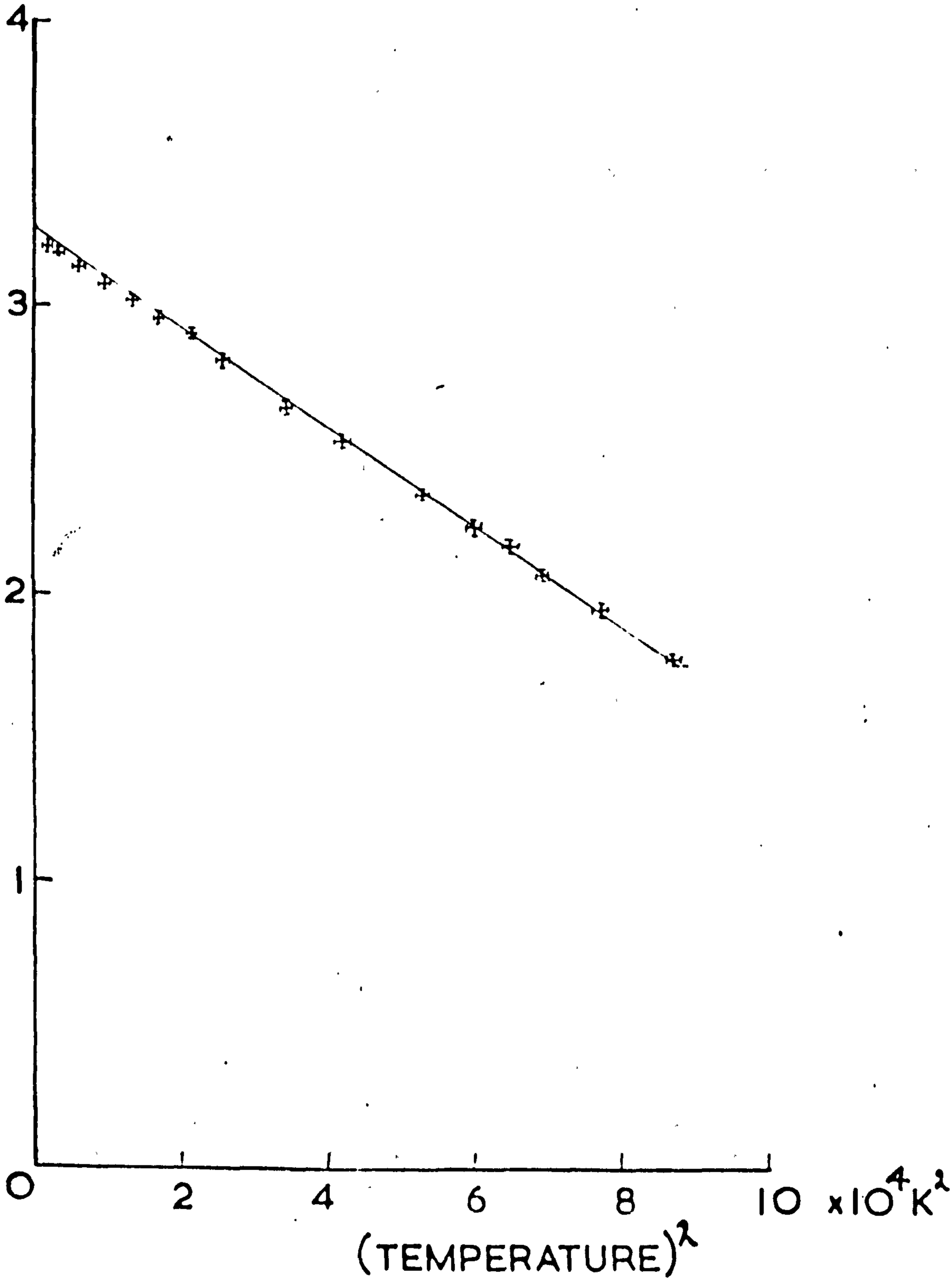


FIG. 4.7

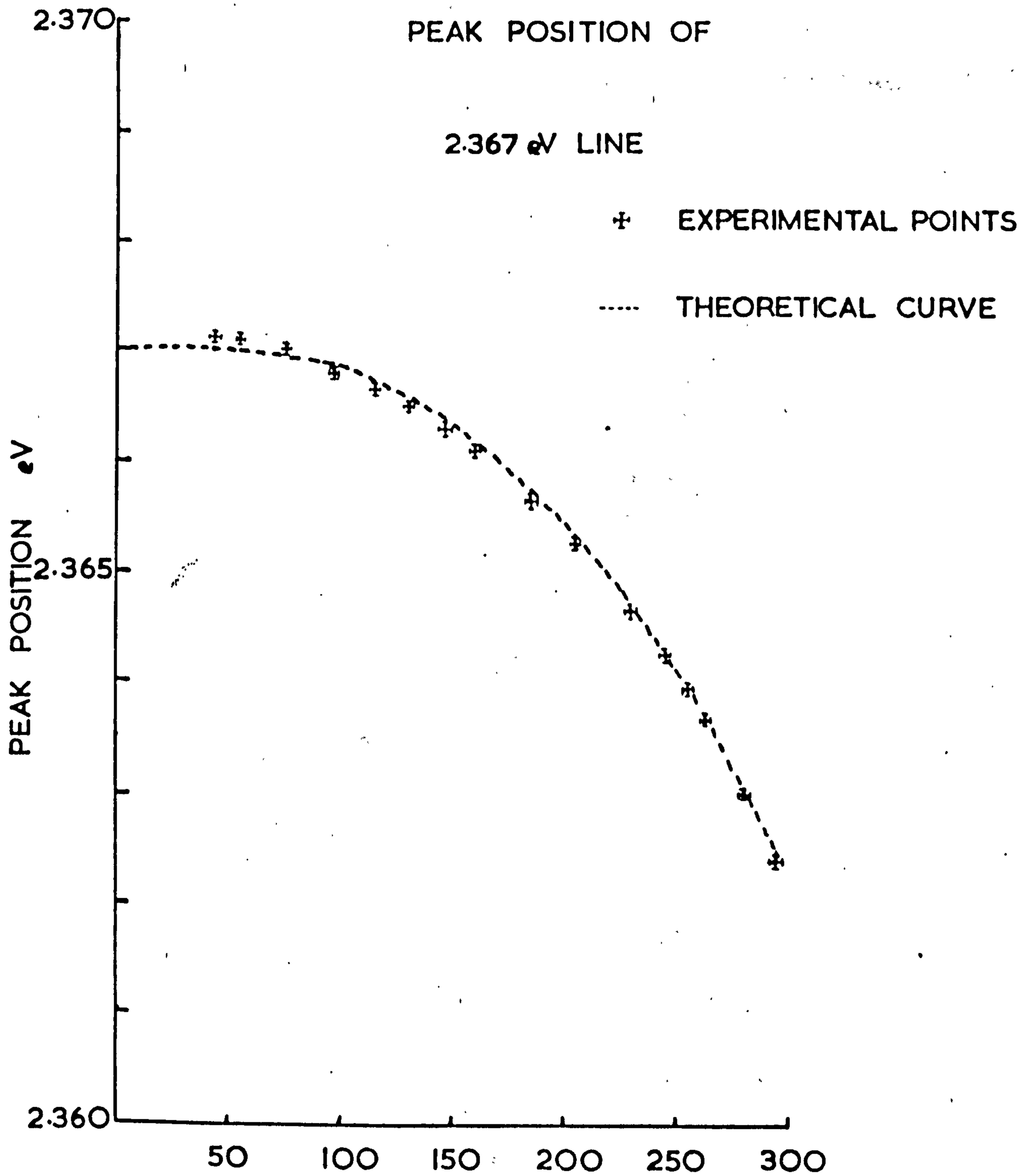
PEAK POSITION OF
2·367 eV LINE
EXPERIMENTAL POINTS
THEORETICAL CURVE
PEAK POSITION eV
2·370
2·365
2·360
50
100
150
200
250
300
TEMPERATURE K

FIG. 4.8

# TEMPERATURE DEPENDENCE OF WIDTH OF 2.367 eV LINE IN 71/134/D

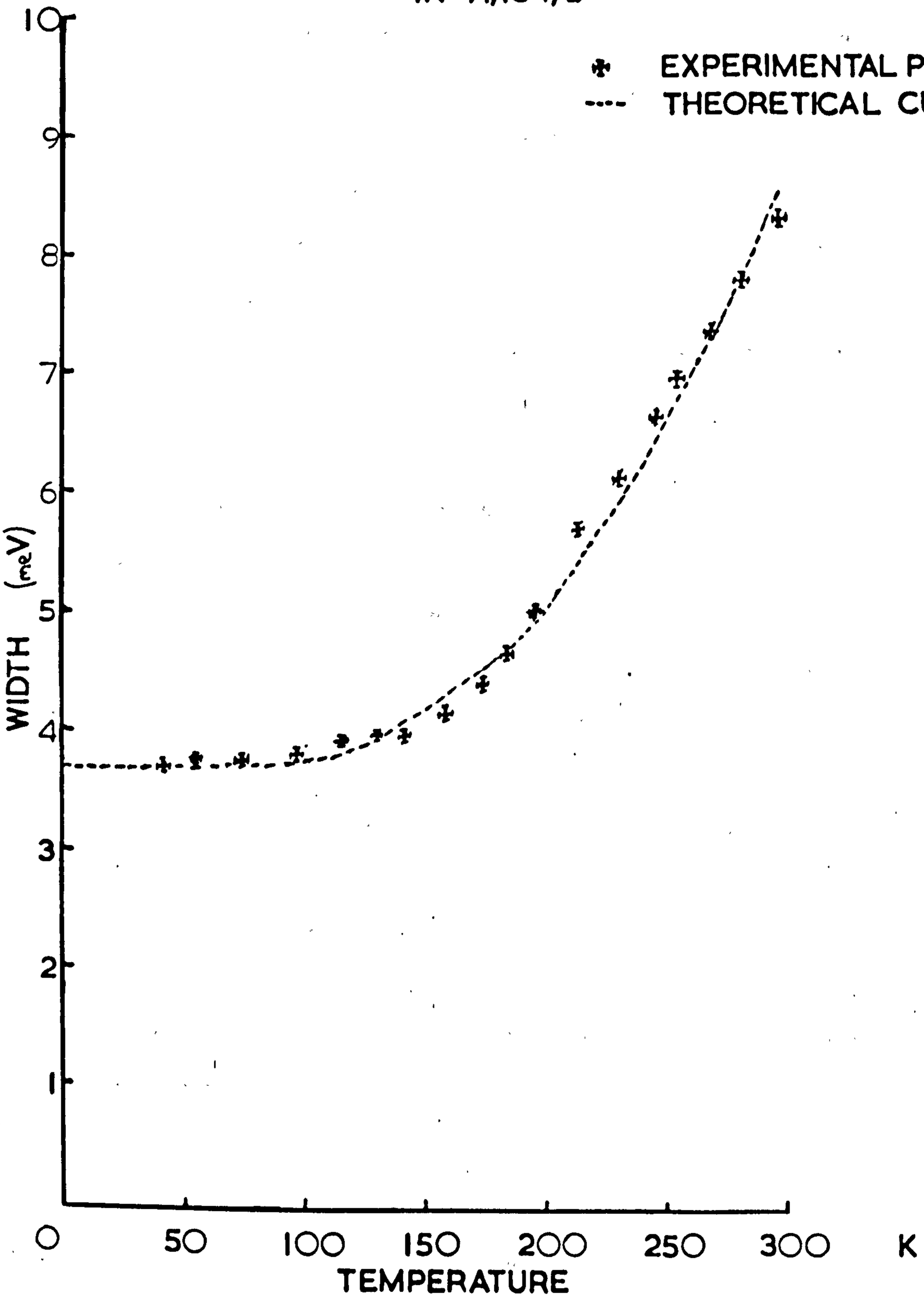


FIG. 4.9

65 meV is once more found to best represent the experimental data. The value of the low temperature line width is specimen dependent, being a function of the varying strain fields from crystal to crystal. However, the form of fig. 4.9 was observed in synthetic and natural type Ib diamond, the former yielding the particular results of fig. 4.9.

The phonon contribution to the width of the zero phonon line is shown in fig. 4.10, as derived from the theory of Maradudin. The theory predicts a $T^2$ variation of the phonon broadening at high temperatures, and such a result is depicted in fig. 4.11.

The analysis of the temperature dependence of the 2.367 eV system has thus shown the vibronic nature of the system to be well represented by a Debye distribution of phonons with a cut off at $\hbar\omega_D$ = 65 meV, corresponding to a Debye temperature of 750K. This Debye temperature compares well with those obtained for other such vibronic systems in diamond, e.g. 1200K for the GRI system. The Huang-Rhys factor S is calculated to be 1.5 from the above analysis, which is rather below the range S = 2 to S = 10 typically found for many vibronic systems in diamond.

## Sec. 4.7 Conclusion.

A previously undetected absorption system having a zero phonon line at 2.367 eV at 80 K has been observed in natural and synthetic type Ib diamond after radiation damage. The occurrence

# PHONON CONTRIBUTION TO WIDTH OF 2·367 eV LINE IN 71/134/D

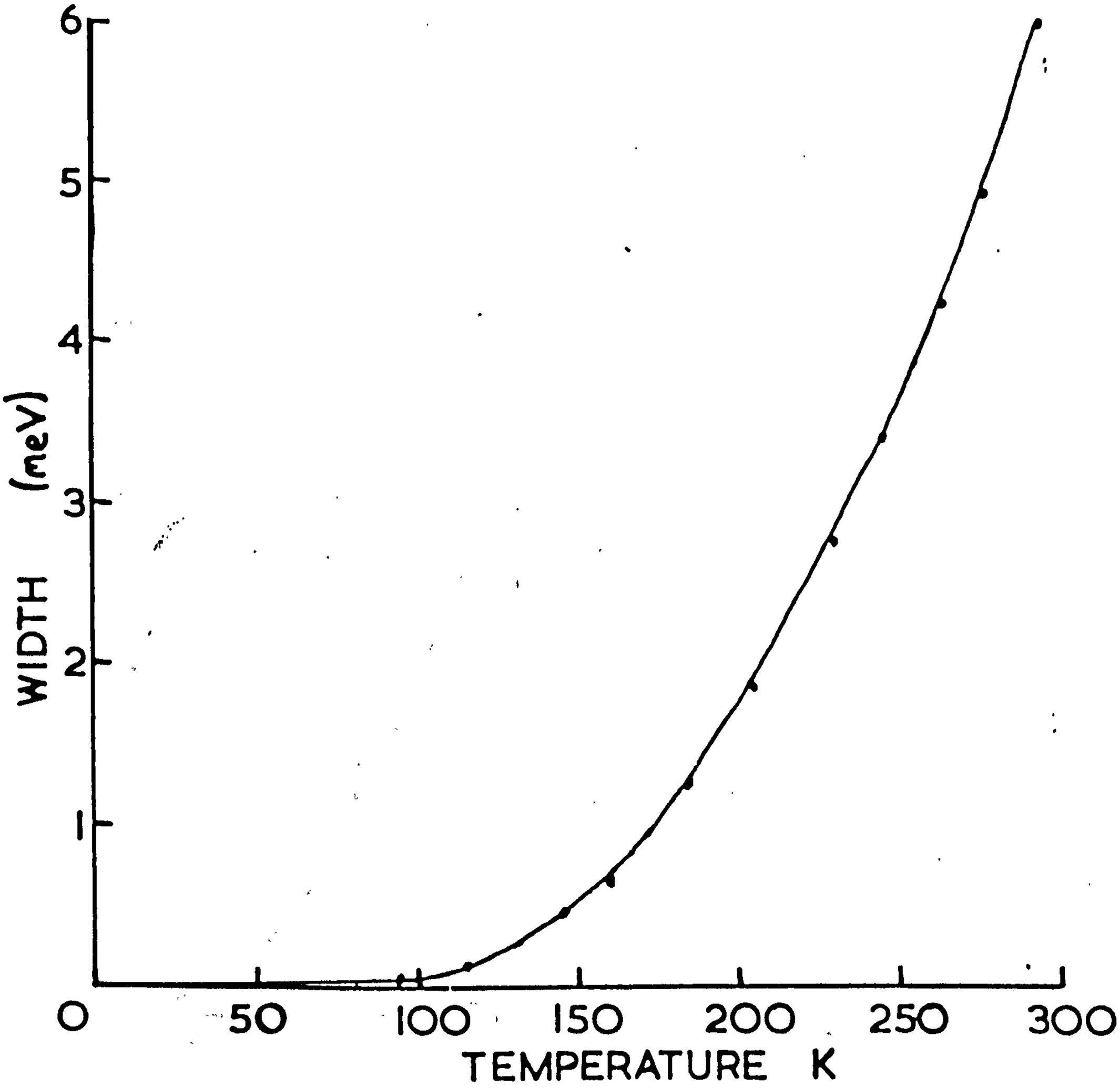


FIG. 4.10

PHONON CONTRIBUTION TO WIDTH
OF 2.367eV LINE IN 71/134/D

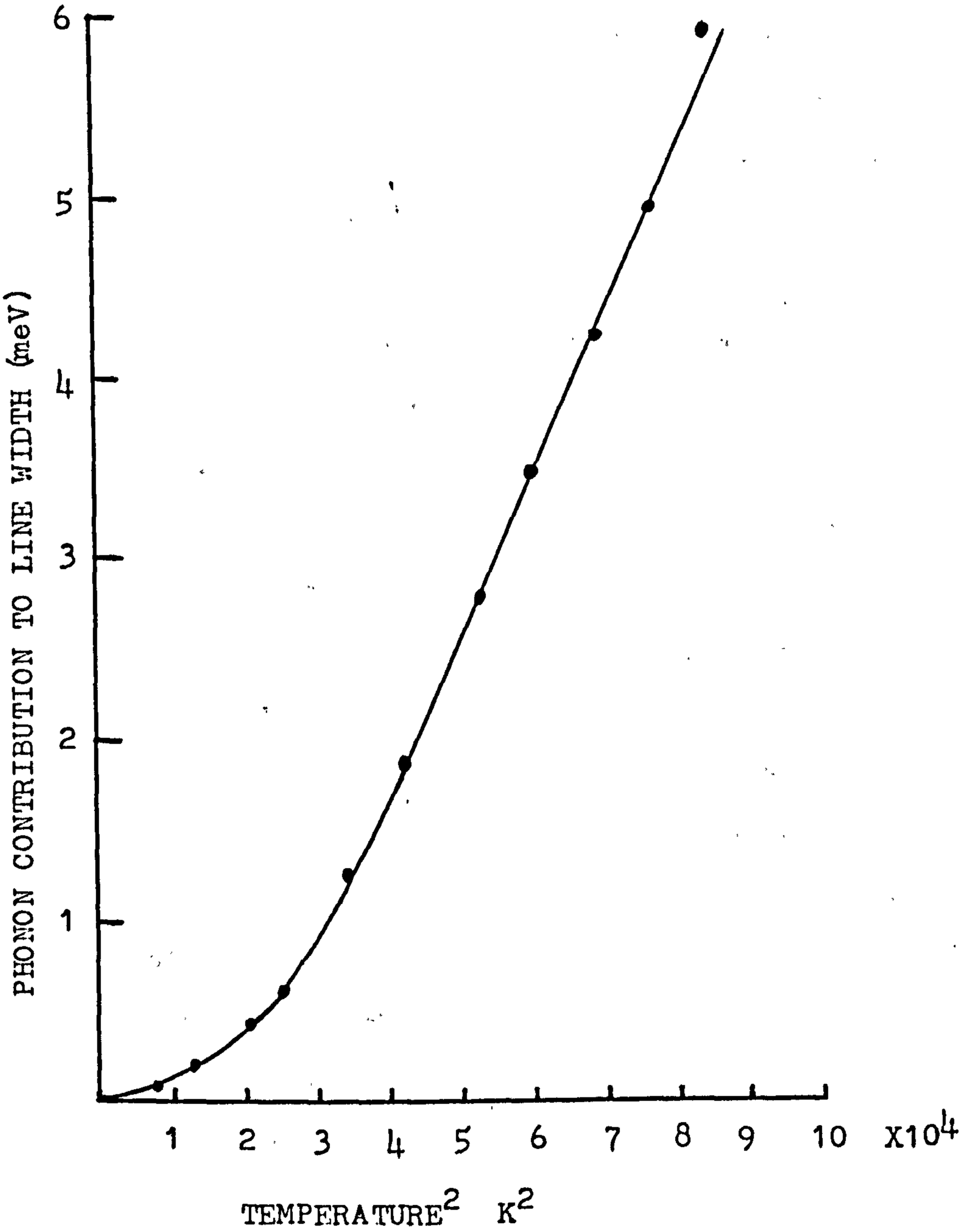


FIG. 4.11

of the system suggests it is produced as a result of isolated nitrogen atoms in the lattice, although the exact nature of the site involved is unknown at present. Interstitial nitrogen atoms convincingly demonstrate the characteristics of the NDI system and thus such a site is unlikely to be the cause of the 2.367 eV transition.

The centre involved has been found to take part in a photon stimulated charge transfer, being ionised by radiation of energy 2.367 eV. Charge has been found to be restored to the centre in the absence of radiation falling on the diamond, and the relative rates of repopulation at temperatures of 5K and 80K suggest thermal repopulation is entirely responsible for the process. As a result of the depopulation of 2.367 eV centres several features in the absorption spectra of type Ib diamonds below a photon energy of 2.367 eV are seen to be enhanced, but no satisfactory quantitative model for the charge transfer process has been found.

The coupling of the electronic structure of the defect involved,to the lattice, has been found to be not atypical of other vibronic systems in diamond, a Debye approximation of phonon distribution fitting the experimental data quite well. Studies into the physical nature of the defect will be of value in determining the dependence of the system upon nitrogen.

## Chapter 4

## References


| | | |
|---|---|---|
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# Chapter 5

## The thermal annealing of radiation damage products in natural type Ia and type Ib diamonds.

### Sec. 5.1 Historical.

This chapter deals with measurements carried out in order to determine the mode of production of optical centres in natural type I diamonds as a result of the thermal annealing of defect centres produced in such diamonds by radiation damage. The main optical systems produced by annealing, and which were studied in the present work, were the H3(503 nm) and H4(496 nm) absorption systems in type Ia diamond (Clark et al, 1956) and the 1.945 eV absorption system in type Ib diamond (du Preez, 1965). The production of these centres was viewed in terms of the rate of thermal annealing of GRI and NDI centres produced in both types of diamond by radiation damage.

Previous studies of thermal annealing in diamond have been carried out, notably by Palmer (1961) and du Preez (1965), but there is some conflict between the results of these workers, and a reappraisal of the process of annealing seems appropriate, particularly in view of different interpretations being made of the nature of the NDI centre by du Preez (1965) and by Davies and Lightowlers (1970).

Before continuing with the results of the present work, we shall consider, in some detail, the results of Palmer and du Preez.

## Sec. 5.2.1 The results of Palmer.

This author carried out extensive, controlled isothermal and isochronal annealing measurements on natural type Ia diamonds, examining in particular the annealing rates of GRI centres as exhibited by the reduction of absorption by the GRI system. Palmer found that a product of thermal annealing was an absorption band between 2.1 eV and 2.8 eV, which was always very weak. This band was termed the TH5 band, and Palmer established an extremely good linear relationship between reduction of the GRI system, and production of the TH5 band, the actual rate of GRI reduction being temperature dependent. Such a linearity is to be expected if a single defect migrates to an impurity, or second defect, to produce a new optical centre. Palmer's study of the kinetics of GRI annealing led him to deduce that the TH5 system was produced as a result of two GRI vacancies combining to form a divacancy which was responsible for the TH5 band.

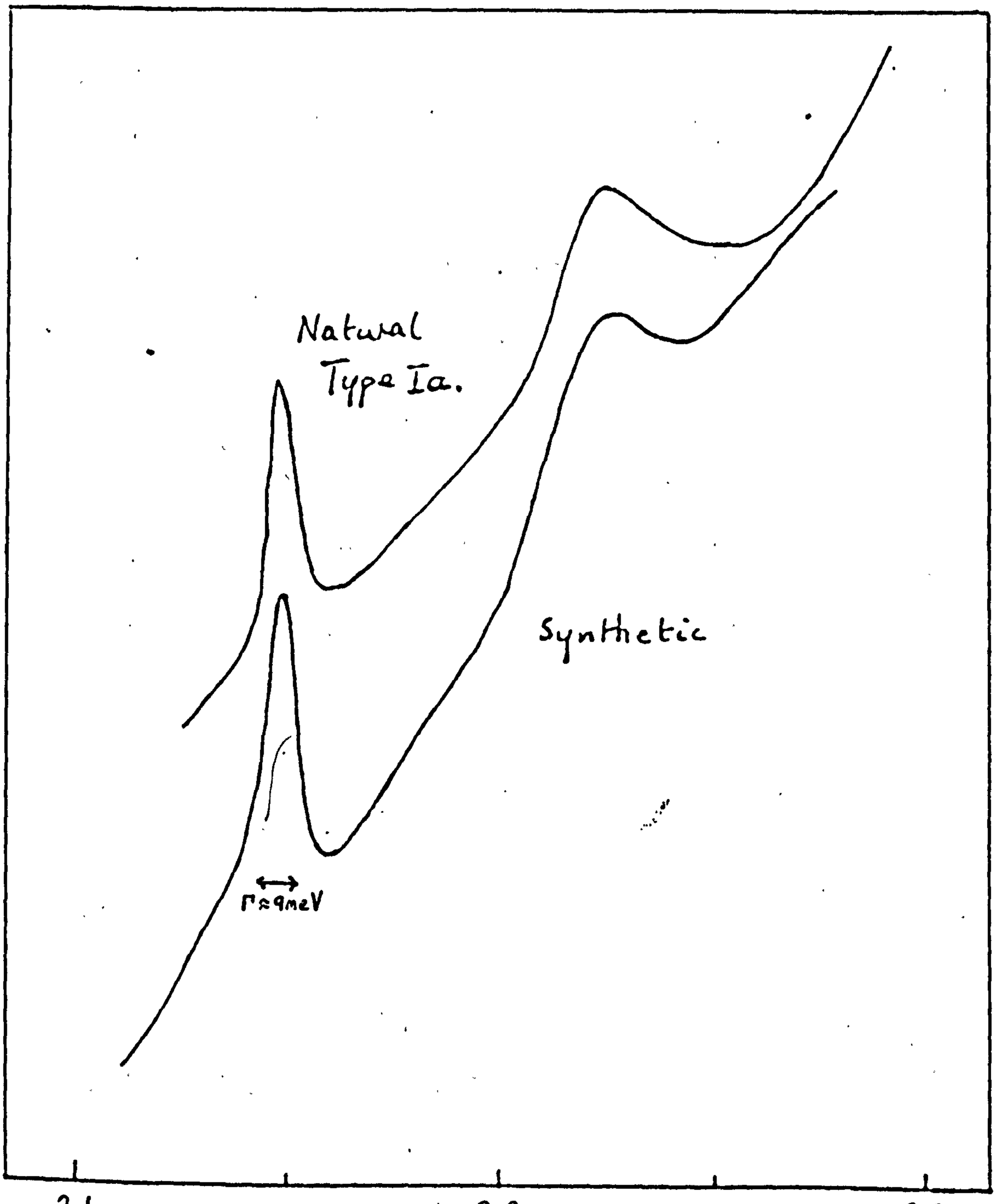
## Sec. 5.2.2 The results of du Preez.

In considering the results of du Preez it is necessary to consider the interpretation of the nature of the NDI centre held at that time. The centre was considered to be an interstitial carbon atom held at the dominant form of nitrogen impurity i.e. at nitrogen "platelets" in type Ia diamond and at isolated nitrogen atoms in type Ib diamond.

The isothermal annealing measurements of du Preez were concerned with the reduction of the GRI and NDI optical absorption systems, and the production of the 640 nm band in type Ib diamond and of the H3 and H2 absorption systems in type Ia diamond. The H2 system was observed to have a weak zero phonon line at 1.2 eV and associated phonon structure. The system was not, however, observed in all type Ia diamonds after annealing. It was observed that, in type Ia diamond, the H3 and GRI systems could be enhanced, at the expense of the H2 and NDI systems, by unfiltered radiation from a mercury discharge lamp. This process could be reversed by heating the specimen. A similar effect was observed between GRI and NDI systems in type Ib diamond, although the 640 nm band was apparently unaffected. The processes were attributed to charge transfer between various centres involved, the maximum absorption detected for any one system being representative of the number of centres producing the system.

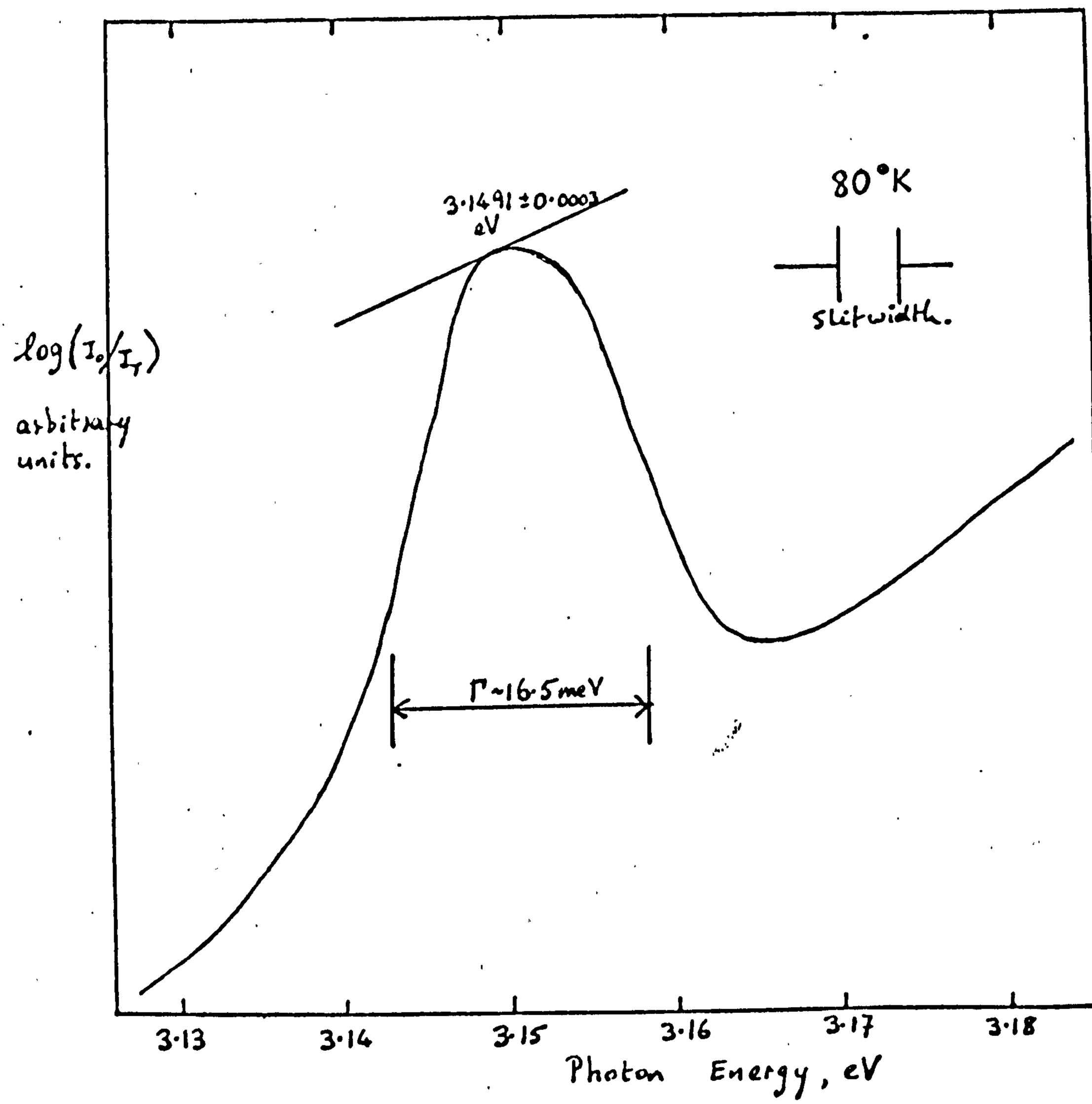
The NDI zero phonon line at 3.149 eV was observed to be similar in natural type Ia and synthetic type Ib diamonds, but the line was considerably wider in natural type Ib diamond. A similar observation was made by Davies (1969) whose typical results are shown in fig. 5.1 and 5.2. Davies suggested the lower linewidth was associated with non-isolated nitrogen, which is present in small quantities in synthetic diamonds.

Typical results obtained by du Preez for the annealing of the GRI and NDI centres in type Ia diamonds are shown in




Comparison of ND1 centres in a natural type Ia diamond and in a synthetic diamond.

FIG. 5.1




NDI in a natural type Ib diamond after 'room temperature' irradiation by 2 MeV electrons and 47 hour at 300 degrees Kelvin.

FIG. 5.2

fig 5.3, recorded for two such diamonds D12 and D13. Diamond D12 illustrates the similar annealing rates of the systems whilst D13 shows that the H3 system continues to grow until the NDI system is no longer observable. Similar behaviour was observed for production of the H2 system in those few specimens in which it was produced. Such results would appear to suggest that the NDI centre is responsible for production of both H2 and H3 systems, presumably in conjunction with two other defector impurity centres. It was argued, however, that GRI centres were responsible for H2 and H3 production, there being a stock of optically inactive GRI centres which were undetected in absorption. The annealing curves showed, however, that a constant fraction of about 20% of GRI centres could be rendered optically inactive by heat treatment, and, consequently, as the number of optically active GRI centres tends to zero, so also does the number of inactive centres. It has been shown by Davies (1974) that the shape of a partially annealed GRI line is unaltered during enhancement of the line by ultra-violet radiation, further suggesting that optically active and inactive GRI centres anneal at the same rate, since the GRI line shape is caused, in part, by the proximity of GRI centres to nitrogen in the lattice. Such evidence conflicts with the interpretations made by du Preez of H2 and H3 production. It was suggested that the H3 system was produced by GRI vacancies migrating to nitrogen platelets whilst H2 centres were the result of GRI vacancies being trapped at NDI centres. The unlikelihood of the combination (NDI + vacancy) when the NDI centre was composed of an isolated nitrogen atom and an interstitial carbon atom was

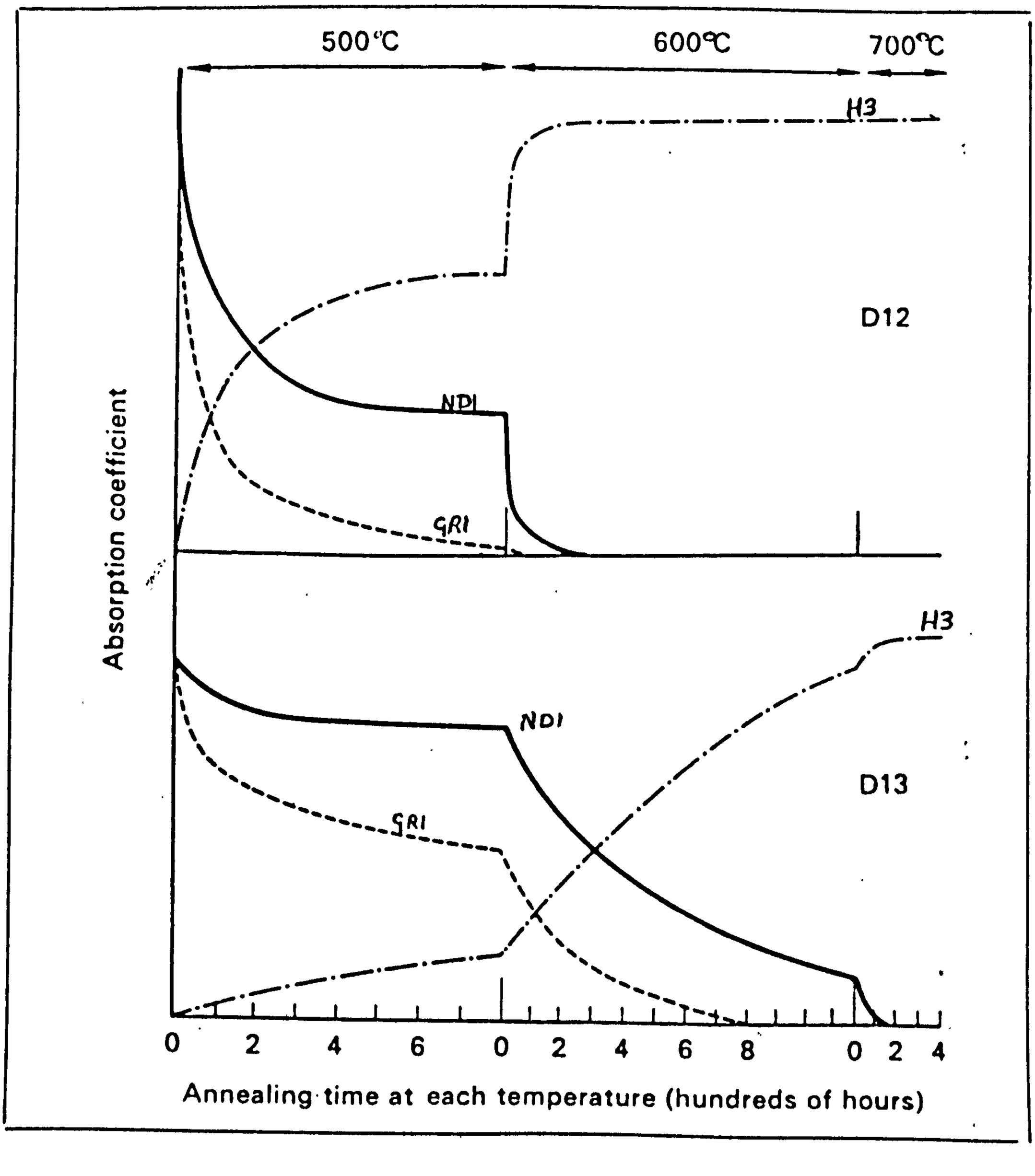

500°C
600°C
700°C
H3
D12
NDI
SRI
H3
NDI
SRI
D13
Absorption coefficient
0 2 4 6 0 2 4 6 8 0 2 4
Annealing time at each temperature (hundreds of hours)

FIG. 5.3

proposed as the reason for the H2 system not being formed in type Ib diamond. This does not, however, account for the H2 system not being observed in all type Ia diamonds of similar NDI and GRI concentrations.

No graphical results were presented by du Preez for the annealing of type Ib diamond but the numerical results suggest production of the 640 nm band only after both GRI and NDI systems had annealed out. This, again, was interpreted in terms of optically inactive GRI centres being trapped at isolated nitrogen atoms to produce 640 nm centres.

It is obvious then that a re-examination of the annealing of radiation damage centres in diamond is required particularly in the light of there being more than one form of nitrogen impurity in type Ia diamond, (Davies and Summersgill 1973), and as a result of the present interpretation of the NDI centre.

## Sec. 5.3 Present Work: General.

The present work was carried out using three natural type Ia diamonds A3, A4, and A6, of nitrogen contents 200ppm, 660ppm, and 1350ppm respectively, and one natural type Ib diamond of nitrogen concentration about 500ppm. The optical systems monitored were the GRI, NDI, H3, and H4 systems in type Ia diamonds, and the GRI, NDI, and 640nm systems in the type Ib diamond. In none of the type Ia diamonds was the H2 absorption system observed.

Charge transfer effects stimulated by ultraviolet light and heat were observed, in agreement with du Preez, enhancement of

the GRI system being completed by illumination of a diamond by a 100W mercury lamp for typically 30 minutes, at a specimen temperature of 80K. Following du Preez, it has been assumed that the maximum absorption produced in any system was a true measure of the concentration of centres producing such a system.

The present study has been carried out with the emphasis being placed upon measurement of changes in the zero phonon lines of the relevant systems, rather than on complete absorption bands, as studied by du Preez. Measurement of zero phonon lines allows one to examine changes of line shapes, as well as absorption, whilst having the advantage of avoiding the problem of overlapping absorption bands e.g. H3 and H4. All measurements were carried out at specimen temperatures of 80K. The integrated absorption of a zero phonon line was estimated by measuring the area under the relevant absorption-coefficient curve. The method of counting squares to measure such areas was found to be accurate to 1%.

## Sec. 5.4 Present Work: Type Ia diamond.

The absorption of the NDI zero phonon line produced in type Ia diamonds after nominal room temperature irradiation by 2 meV electrons has been seen to be increased by heating the diamond for several minutes at 400°C. This is attributed to completion of the formation of NDI centres according to the model of Davies and Lightowlers (1970), in which there is a temperature-promoted exchange of site between a nitrogen atom and an interstitial carbon atom. The NDI zero phonon line is seen

to have a tail to lower energies which is suggested by Davies (1974) to be caused by NDI centres being perturbed as a result of their proximity to nitrogen complexes. When annealing commences at about 500°C the low energy tail is seen to anneal out more quickly than the bulk of the zero phonon line, suggesting that the centres responsible can combine more easily with their nitrogen near neighbours than can other NDI centres. The appearance of the NDI zero phonon line immediately after irradiation and after a subsequent period of 10 hours at 500°C is seen in fig. 5.4, as recorded for specimen A3. The intermediate stage, obtained after irradiation followed by a few minutes at 400°C (at which temperature annealing does not occur) is not shown. This stage showed a line shape similar to that observed immediately after irradiation, but with a peak height some 25% higher.

We shall now discuss the individual results of the diamonds investigated.

Sample A3

The absorption curves for diamond A3 are shown in fig. 5.5. It can be seen that both H3 and H4 systems were produced in the diamond, the ratio of their intensities being about 5.5 to 1. The GRI system annealed completely after 4 hours at 700°C, whilst the NDI system was observed until a period of 30 hours at 700°C had elapsed. Both H3 and H4 systems continued to grow after extinction of the GRI system, provided the NDI system could still be detected.

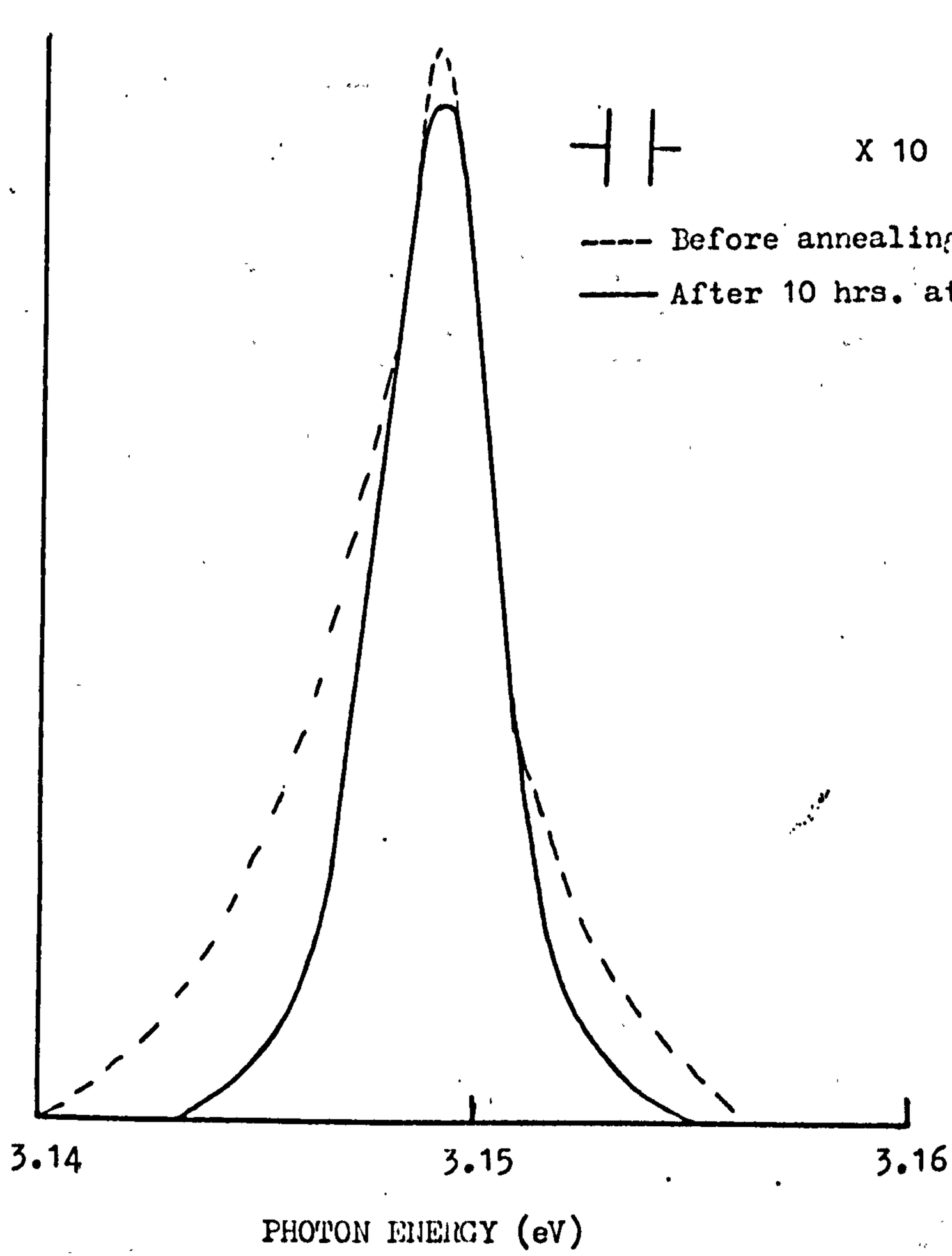

ND1 ABSORPTION IN DIAMOND A3
X 10
---- Before annealing
—— After 10 hrs. at 500°C
ABSORPTION
3.14
3.15
3.16
PHOTON ENERGY (eV)

FIG. 5.4

SAMPLE A3

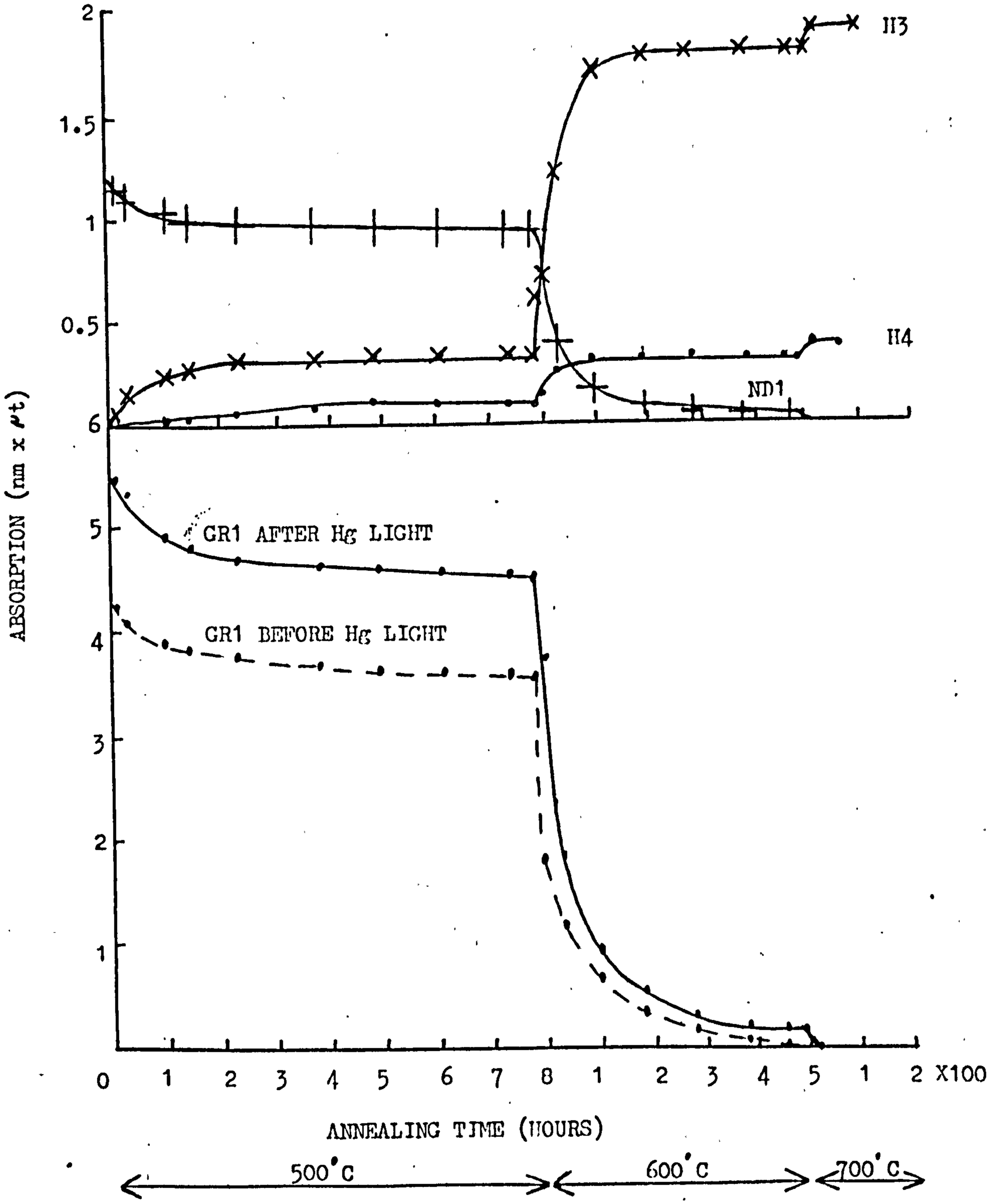



FIG. 5.5

In fig. 5.6 the strengths of the H3 and H4 zero phonon lines are shown as a function of GRI absorption. It is seen that quite a good linear relationship exists in each case, the computed best linear fit giving correlation coefficients of 0.97 in each case.

A similar relationship is shown between H3, H4 and NDI systems in fig. 5.7. Again the linear fits are very good, giving correlation coefficients of 0.99.

Comparison of fig. 5.6 and 5.7 would suggest that the NDI centre is more likely to be responsible for production of the H3 and H4 system, which are known to be produced by the same defect migrating to nitrogen complexes (Davies and Summersgill 1973), than is the GRI centre. The problem is considerably complicated, however, by the similar annealing rates of the GRI and NDI centres.

Sample A4.

The results of annealing diamond A4 are shown in fig. 5.8. The rates of GRI and NDI reduction are much as for diamond A3, but in this case, no H4 absorption was produced. The GRI system annealed completely after 20 hours at 700°C, whilst the NDI system disappeared after 40 hours at 700°C. Once again, H3 production was observed only during the presence of the NDI system.

Fig. 5.9 shows the H3 system as a function of the GRI and NDI systems. The H3/GRI best linear fit gives a correlation coefficient of 0.97 whilst the H3/NDI fit produces a correlation coefficient of better than 0.99.

# SAMPLE A3

## DEPENDENCE OF H3&H4 ON GRI

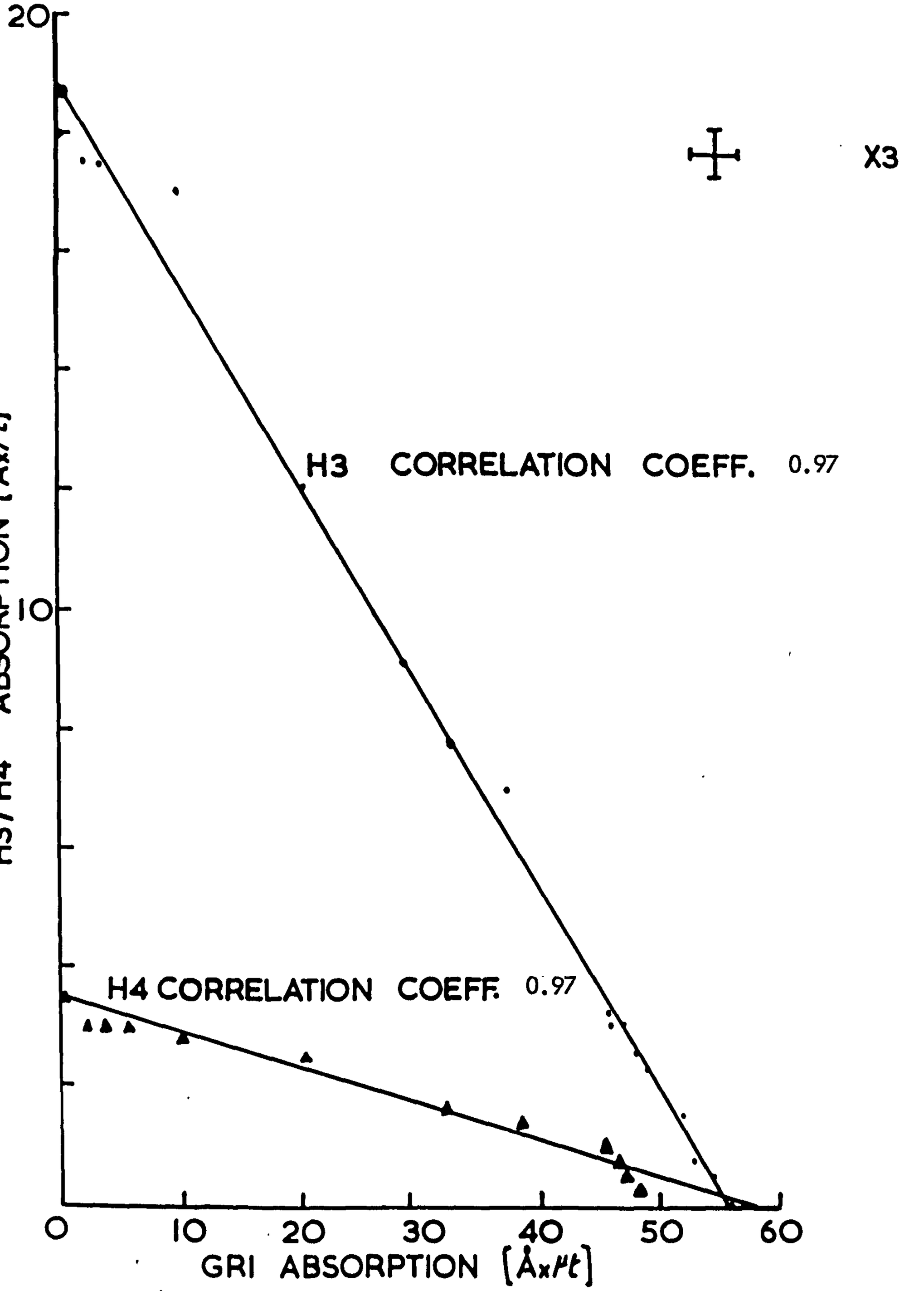



FIG. 5.6

# SAMPLE A 3
# DEPENDENCE OF H3&H4 ON NDI

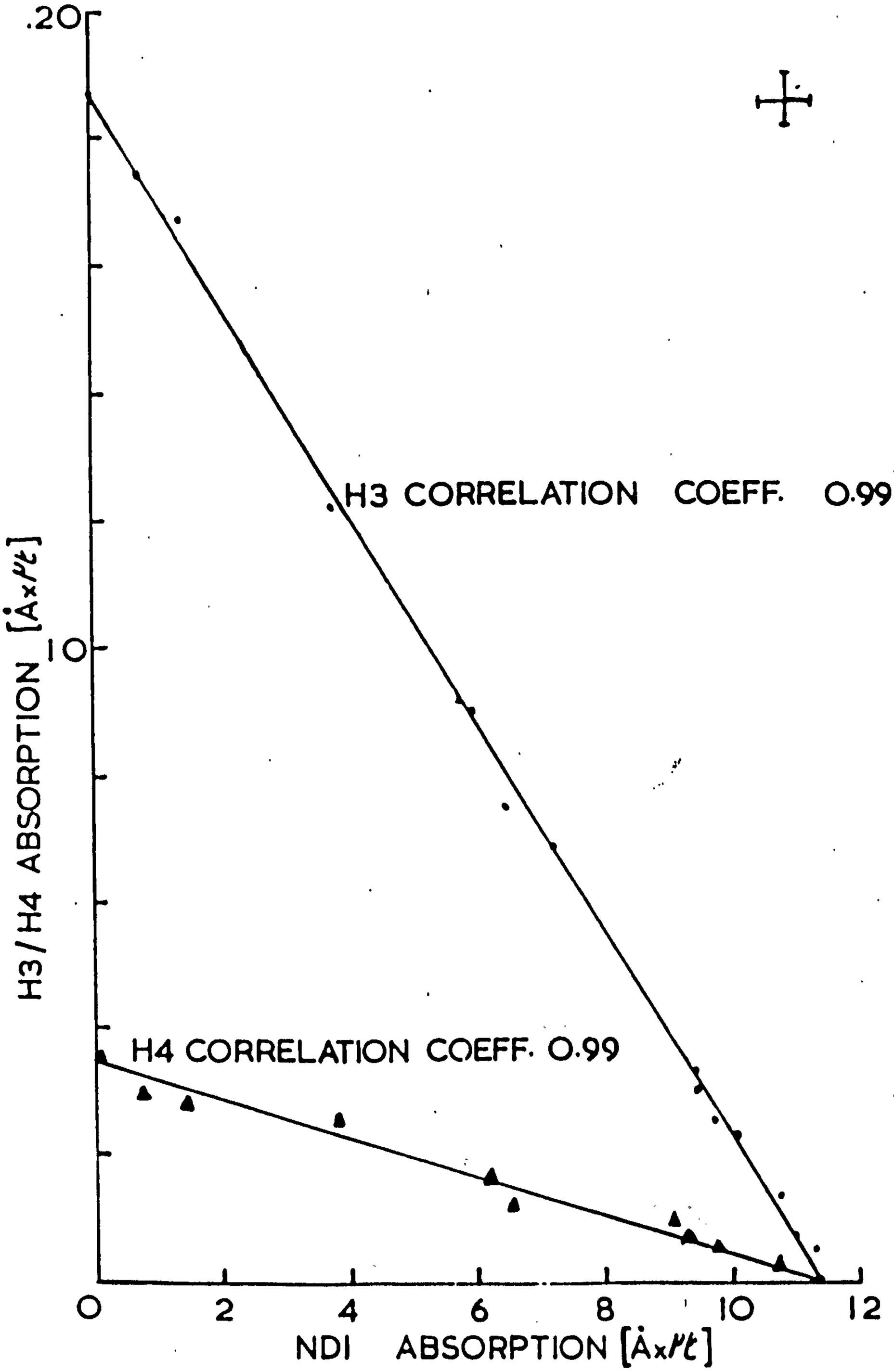



FIG. 5.7

SAMPLE A4

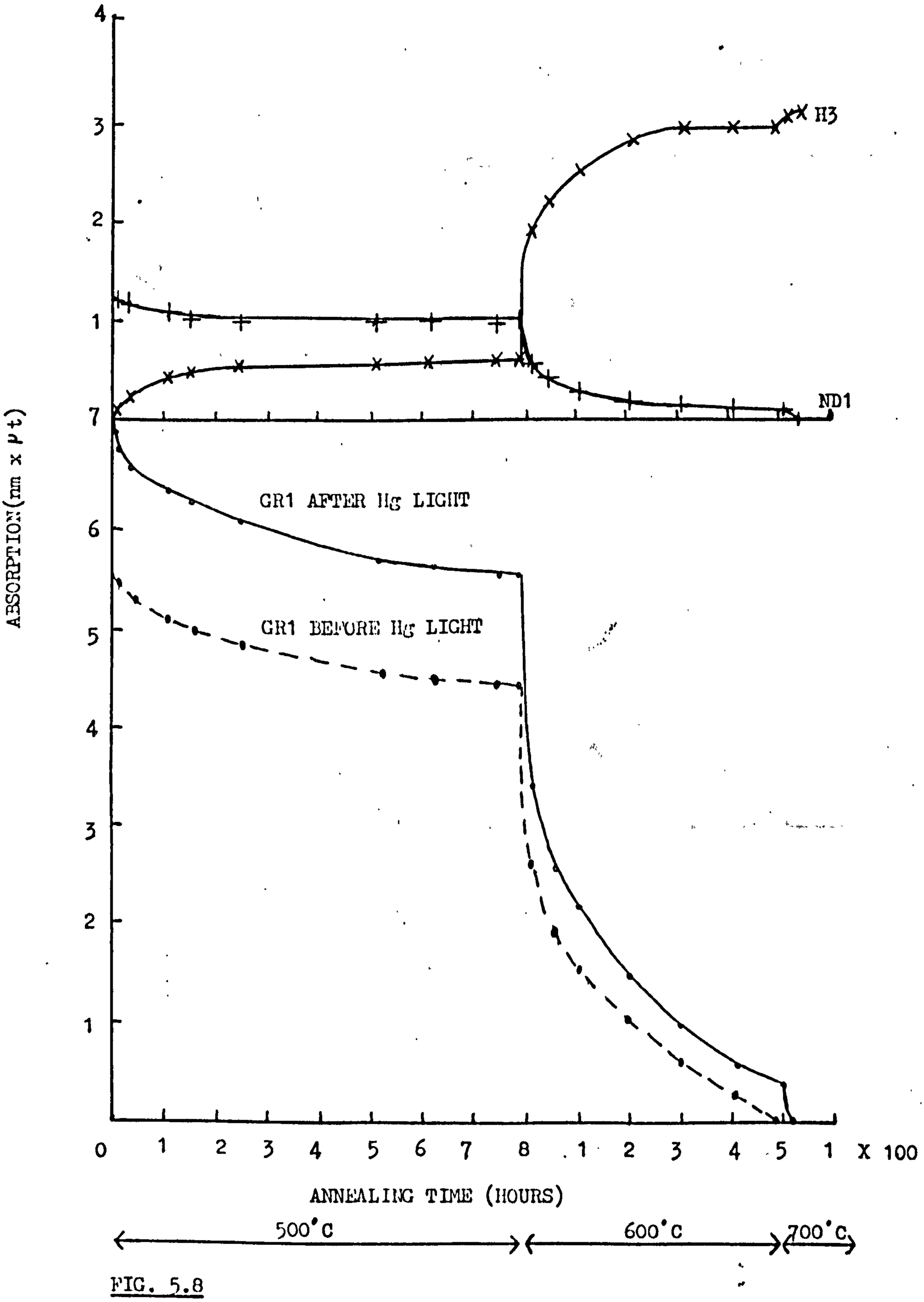



FIG. 5.8

SAMPLE A4

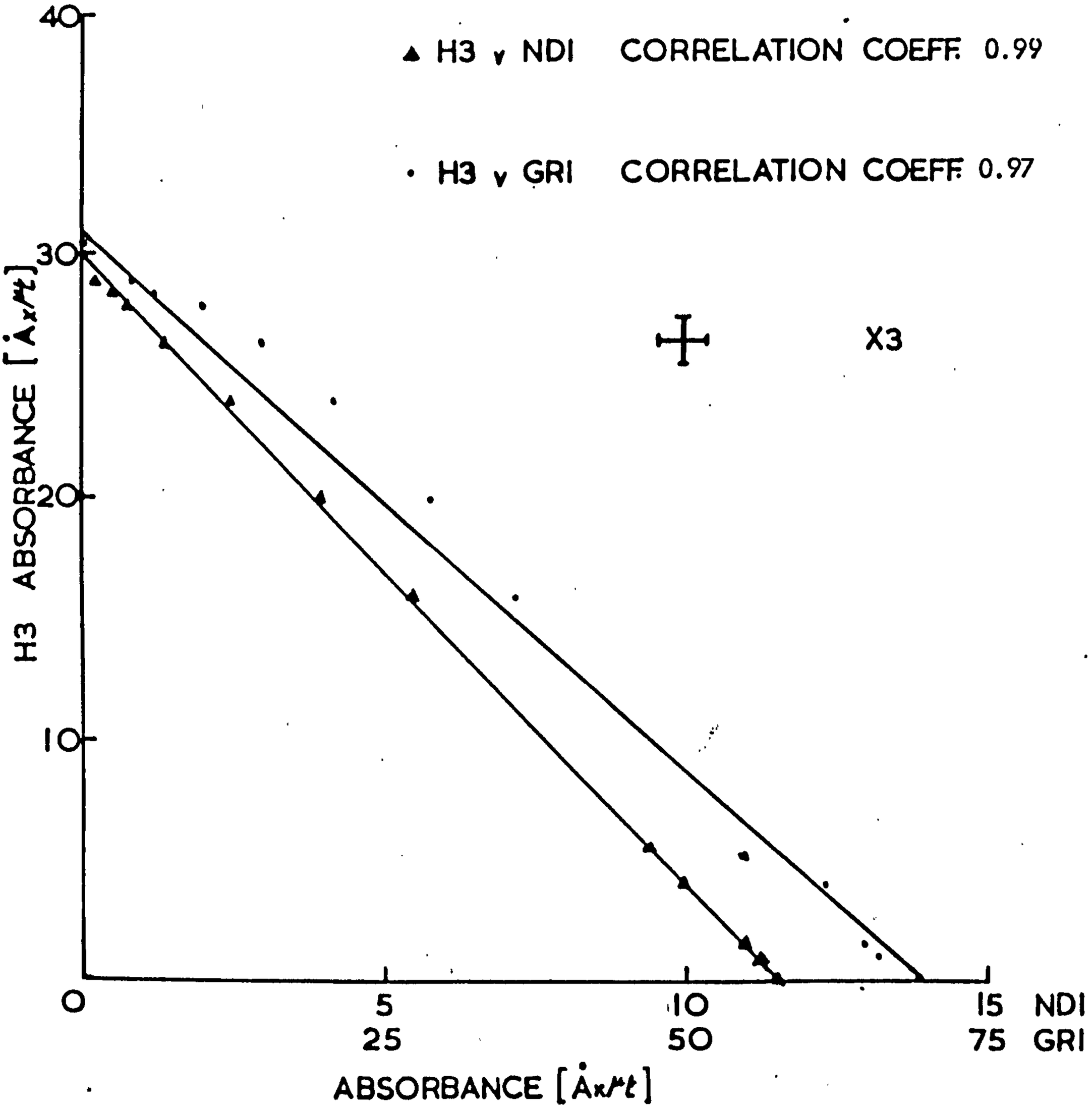



FIG. 5.9

The results of diamond A4 thus also suggest that NDI centres are responsible for formation of the H3 absorption system.

Sample A6.

The annealing rates of the NDI and GRI systems observed in diamond A6 are shown in fig. 5.10. The GRI system annealed completely after 20 hours at 700°C and the NDI after 40 hours at 700°C. As with diamond A3, both H3 and H4 systems were produced, both continuing to increase in strength as long as NDI absorption was observable. Fig. 5.11 shows the correlation between the GRI system and the H3 and H4 systems. The H3/GRI correlation is 0.96 whilst the H4/GRI correlation is 0.98. The H3 and H4 systems are shown as functions of the NDI system in fig. 5.12. The H3/NDI correlation obtained is 0.98 whilst the H4/NDI correlation is better than 0.99.

Again the evidence suggests that the NDI centres are responsible for production of H3 and H4 centres in type Ia diamond.

It has been seen that the NDI and GRI absorption systems in type Ia diamond anneal at similar rates and that, consequently, each can be quite well correlated with the growth of H3 and H4 systems in such diamonds. The linear best fits to the data of the present work have been provided by a linear regression computer program aarried out on a Hewlett Packard 9810A desk calculator. For any given diamond the number of points used in both GRI and NDI correlations were equal.

SAMPLE A6

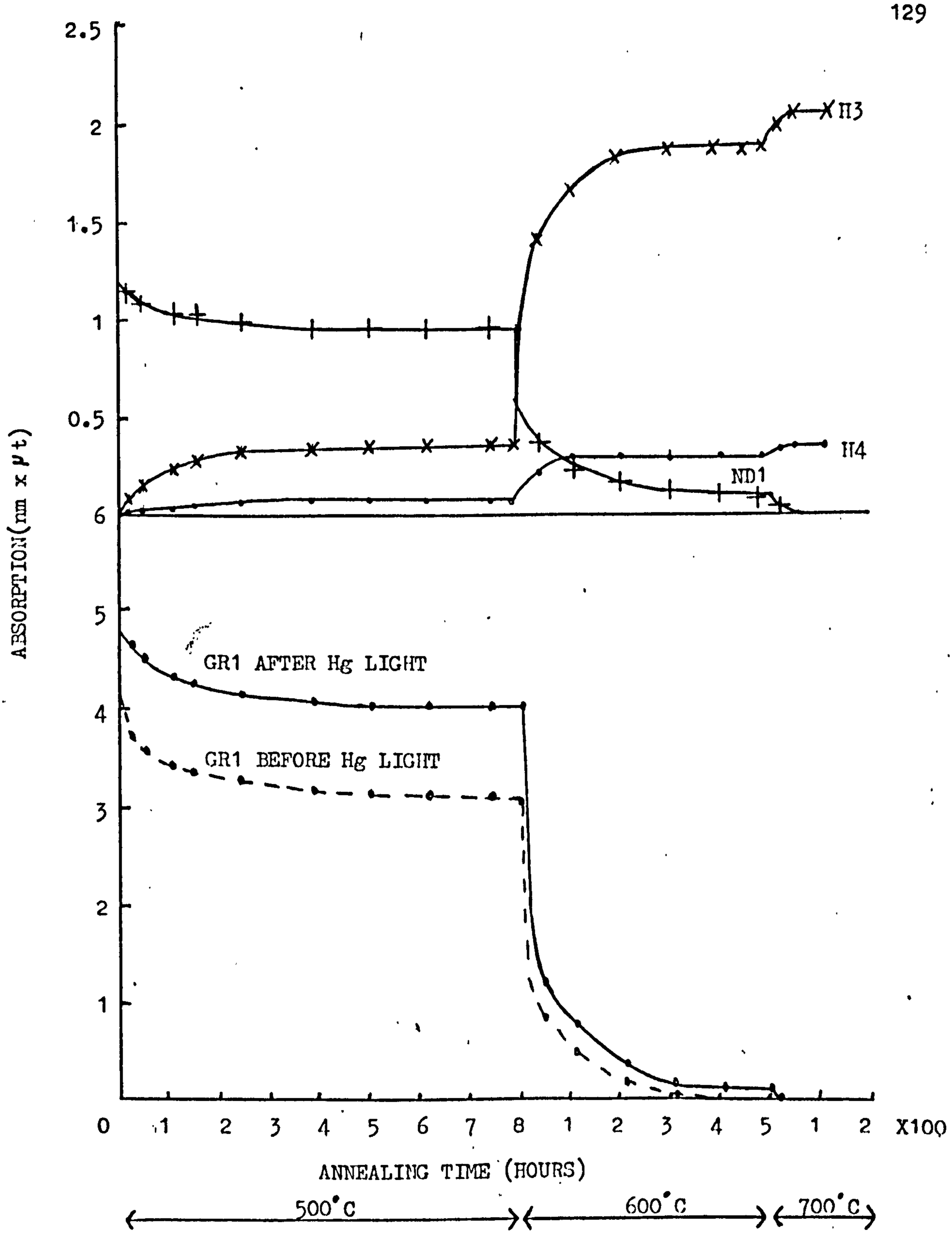



FIG. 5.10

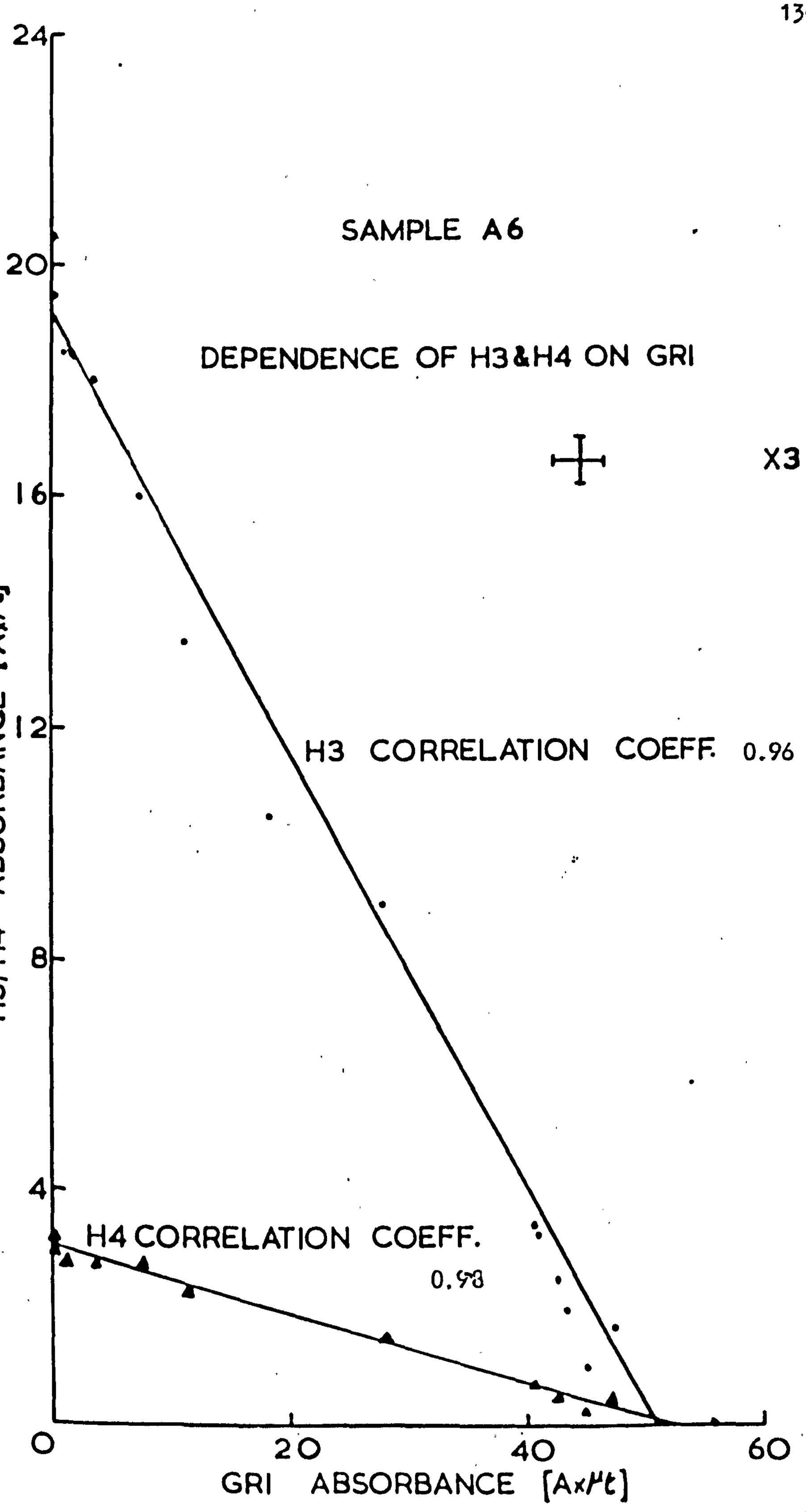

SAMPLE A6
DEPENDENCE OF H3&H4 ON GRI
X3
H3 CORRELATION COEFF. 0.96
H4 CORRELATION COEFF. 0.93
H3/H4 ABSORBANCE [A x μt]
GRI ABSORBANCE [A x μt]
24
20
16
12
8
4
0
20
40
60

FIG. 5.11

SAMPLE A6

DEPENDENCE OF H3&H4 ON NDI

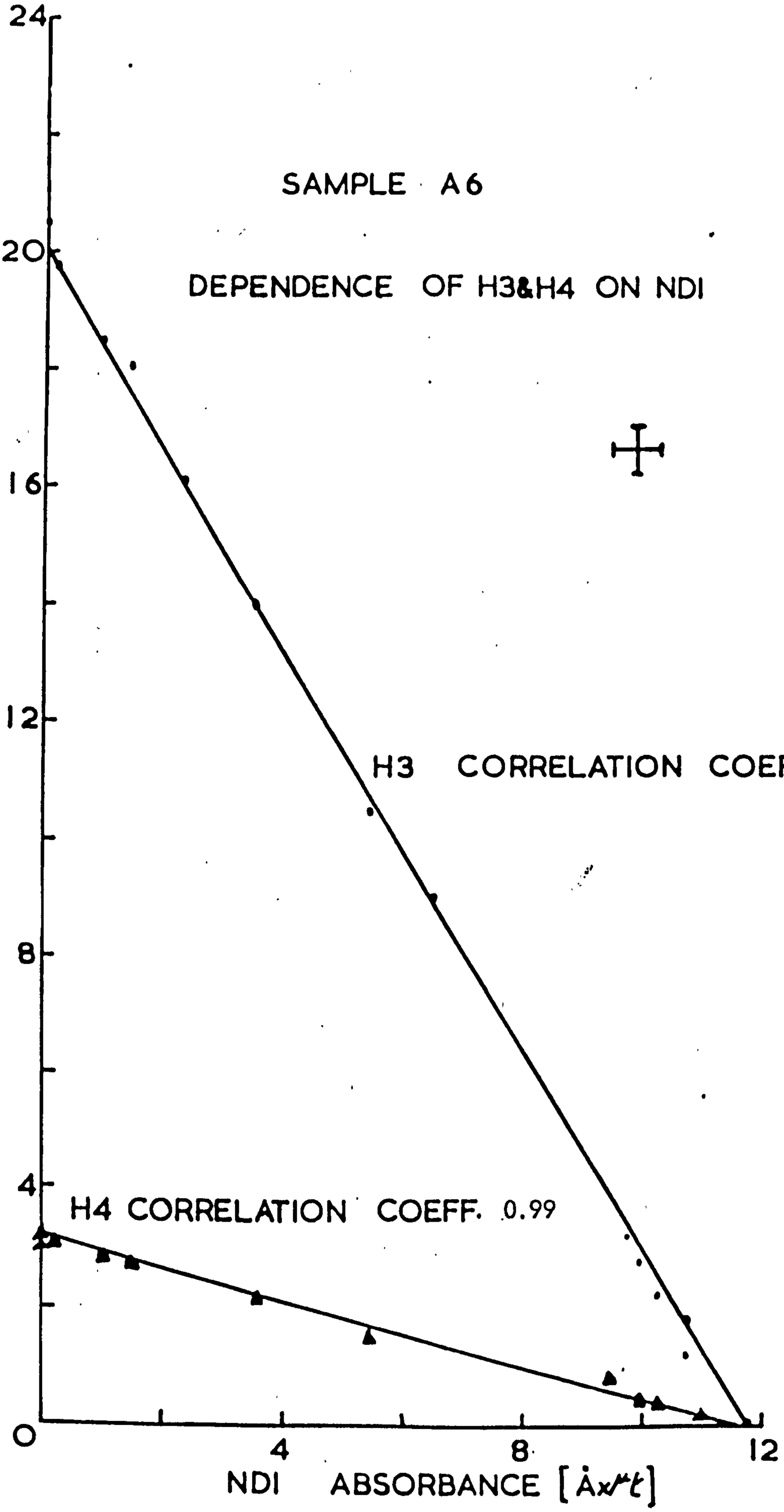



FIG. 5.12

In addition, provided the signal $I_t$ transmitted through the diamond is never less than about 20% of the signal $I_o$ falling on the diamond, then although the percentage errors inherent in measurement of the integrated absorptions of the H3, H4, GR1, and ND1 lines change during annealing as a result of the strengths of these lines changing, the absolute errors in such quantities do not alter significantly. Such was the case in the present work. Hence, equal degrees of confidence can be expressed in the correlations achieved for the GR1 and ND1 systems in relation to production of H3 and H4 systems. Thus, the present results suggest that it is the ND1 interstitial nitrogen centre which, by migration to the A and B types of nitrogen impurity, produces the H3 and H4 absorption systems in type 1a diamond. This is particularly so since the better ND1 correlation exists over a wide range of annealing temperatures.

---

Whilst the above analysis suggests that, within a given diamond, NDI centres do not migrate <u>preferentially</u> to centres other than the A or B forms of nitrogen, there is no evidence concerning whether or not NDI centres are actually involved in the production of optical systems other than H3 or H4 centres. Such evidence can be provided, however, by the comparison of the effects of annealing in several diamonds.

Let us assume (following Davies and Summersgill 1973), that there are two main types of impurity nitrogen aggregates in type Ia diamond, the A and B forms, and that any other nitrogen impurity is present only in relatively small quantities. Let us also assume that a single defect, D, is responsible, by migration to A and B centres, for production of H3 and H4 centres, as shown by the above authors. If the number of centres of type D, i.e. $N_D$, is less than the number of aggregates of types A and B, then, provided defect D is not appreciably involved in migration to centres other than A or B, we can write

$$N_D = N_{H3} + N_{H4} \qquad \text{eq. 5.1}$$

where $N_{H3}$ and $N_{H4}$ are the numbers of H3 and H4 centres produced by the complete annealing of D centres. Eq. 5.1 assumes one D type centre is involved in production of each H3 and H4 centre.

Let us designate the absorption per centre of D, H3, and H4, as $k_D$, $k_3$, $k_4$ respectively.

We then have

$$k_D N_D = k_D N_{H3} + k_D N_{H4} \qquad \text{eq. 5.2}$$

$$\text{i.e. } k_D N_D = \frac{k_D}{k_3} (k_3 N_{H3}) + \frac{k_D}{k_4} (k_4 N_{H4}) \qquad \text{eq. 5.3}$$

i.e. initial absorption of defect D =

$$K_A(\text{H3 absorption}) + K_B(\text{H4 absorption}) \qquad \text{eq. 5.4}$$

where $K_A = \frac{k_D}{k_3}$ and $K_B = \frac{k_D}{k_4}$

Let us now draw up a table of the relevant absorptions of the features involved for the three type Ia diamonds involved in this work.

| | A3 | A4 | A6 |
|---|---|---|---|
| NDI Initial Absorption | 1.14 | 1.15 | 1.18 |
| GRI Initial Absorption | 5.60 | 7.00 | 5.61 |
| H3 Final Absorption | 1.88 | 3.03 | 2.05 |
| H4 Final Absorption | 0.34 | 0.00 | 0.32 |

Let us firstly consider the behaviour of the GRI system. Substituting the results of diamond A4, in which no H4 system was produced, into eq. 5.4 yields:-

$$7.00 = 3.03\ K_A \qquad \text{whence} \quad K_A = 2.31$$

Treating A3 and A6 as simultaneous equations yields

$$5.60 = 1.88\ K_A + 3.4\ K_B$$

$$5.61 = 2.05\ K_A + 3.2\ K_B$$

whence $K_A = 1.15$ and $K_B = 10.11$

$$\frac{K_B}{K_A} = 8.79 \qquad \text{or} \quad \frac{k_3}{k_4} = 8.79.$$

It is seen that a considerable difference between the values derived for $K_A$ is produced, suggesting that GRI vacancies cannot be responsible for H3 and H4 production unless large proportions of GRI vacancies are also trapped at centres other than A and B nitrogen complexes, a proposition which will be examined later.

Performing the same analysis for the NDI system in A4 yields

$$1.15 = 3.03\ K_A$$

whence $K_A = 0.38$

The equations for A3 and A6 are:-

$$1.14 = 1.88\ K_A + 0.34\ K_B$$

$$1.18 = 2.05\ K_A + 0.32\ K_B$$

whence $K_A = 0.39$ and $K_B = 1.16$.

Thus $\frac{K_B}{K_A} \sim 3$ and so $\frac{k_3}{k_4} \sim 3$

It is seen that the values of $K_A$ produced in this case are in good agreement, suggesting that NDI centres are indeed responsible for H3 and H4 production along the lines indicated.

We have seen from the work of Davies and Summersgill (1973) that the ratio $\mu_A / \mu_B$ is nearly equal to the ratio $k_3/k_4$ where $\mu_A$ and $\mu_B$ are the absorption coefficients, per unit centre, of the A and B forms of nitrogen aggregate in type Ia diamond at 1282cm $^{-1}$ and $k_3$ and $k_4$ are defined as above. The ratio $\mu_A / \mu_B$ has been calculated as $0.6 < \mu_A/\mu_B < 1.6$ by Davies (1972) and as $3.5 \pm 0.3$ from the results of Sobolev et al (1972). The value of the ratio $k_3/k_4$ derived in the present work hence fits well into the above scheme of results of previous workers.

When errors produced by calculation of absorption coefficients are taken into account, the value of $K_3/k_4$ derived during the present work can be quoted as $1 < \frac{k_3}{k_4} < 5$, the relatively large spread of values being a result of measuring

absorption coefficients of similar magnitude, the errors in such measurements being compounded during the solution of simultaneous equations. Such a range of values for $k_3/k_4$ still compares well, however, with those derived from the results of previous workers.

The above analysis has been carried out on the assumption that there is no third trap to which NDI or GRI centres could migrate during annealing. If one accepts that GRI centres are responsible for production of the TH5 band (Palmer 1961), then a term accounting for this should appear in equation 5.4. However, TH5 absorption is at best extremely weak, and unless this is a result of low oscillator strength, then TH5 centres cannot be present in sufficiently large quantities to restore the imbalance of eq. 5.4 when applied to the GRI system.

The second centre to be accounted for is the H2 centre. Although absorption associated with this centre was not observed during the present work, the results of du Preez (1965) suggest it is produced in some type Ia diamonds provided the NDI system is still observable. Thus, in general, eq. 5.4 could be amended to account for this system, but since H2 absorption is usually extremely weak, it, also, will have little effect upon the above analysis unless the oscillator strength of the system is very low.

Since nitrogen is the predominant impurity in type Ia diamond, and since less than 10% of such nitrogen is present in forms other than the familiar A and B types of aggregate (Davies 1970), it is conceivable that the H2 system is produced by the trapping of NDI interstitials at a form of nitrogen complex

present, at most, in very small quantities. An alternative candidate for H2 production might be the trapping of NDI centres centres at "platelets" in such diamonds.

As a result of no strong optical absorption system being found in type Ia diamond which could be interpreted as evidence for an alternative trap for NDI centres, it is considered that eq. 5.4 can provide a realistic representation of the annealing of the diamonds used in the present work. Consequently, the results of the foregoing analysis strongly suggest that the NDI interstitial, and not the GRI vacancy, is the defect necessary for production of the H3 and H4 absorption systems in type Ia diamond.

It can be seen from the foregoing annealing curves (fig. 5.3, 5.5, 5.8, 5.10), that, at any given temperature, there is a limit to the extent to which both GRI and NDI systems can be annealed out. An increase of temperature, however, is seen to cause a rapid continuation of the annealing process exhibited by these systems. As has been observed previously in this section, the initial stages of NDI annealing are accompanied by reduction of the width of the zero phonon line, interpreted as those NDI centres which are perturbed by their proximity to nitrogen being annealed first. Further annealing is not, however, accompanied by reduction of the NDI zero phonon line width, which would be expected if the siting of NDI centres at various distances from nitrogen (thereby suffering a range of perturbations), were responsible for saturation of annealing at a given temperature. The distribution of NDI centres

at varying distances from nitrogen complexes does not, therefore, apparently account for such saturation effects of the NDI system.

The width of the GRI zero phonon transition does, however, continuously decrease during annealing of this system, and since GRI centres are also predominantly close to nitrogen (Davies 1974), it is suggested that the behaviour of GRI absorption during annealing is attributable to a range of perturbations suffered by the GRI centres as a result of their situations in the lattice.

## Sec. 5.5 Annealing of natural type Ib diamond.

Due to the non-availability of suitable specimens, this survey was confined to measurements upon only one natural type Ib diamond. The decrease of GRI and NDI systems was monitored, along with the increase of the 1.945 eV zero phonon line, representing the 640 nm band. This latter system was the only absorption system observed to increase in strength during annealing in this diamond.

Fig. 5.13 shows the annealing curves obtained for this diamond at 600°C and 700°C. As with the type Ia diamonds, the maximum absorption obtainable as a result of thermochromic effects is taken as representative of the true strength of the system. It is seen that the GRI system annealed out after 40 hours at 700°C whilst the NDI system disappeared after 52 hours at 700°C. The 1.945 eV line appears to follow the changes in the NDI system, being found to increase after extinction of the GRI absorption.

SAMPLE BI

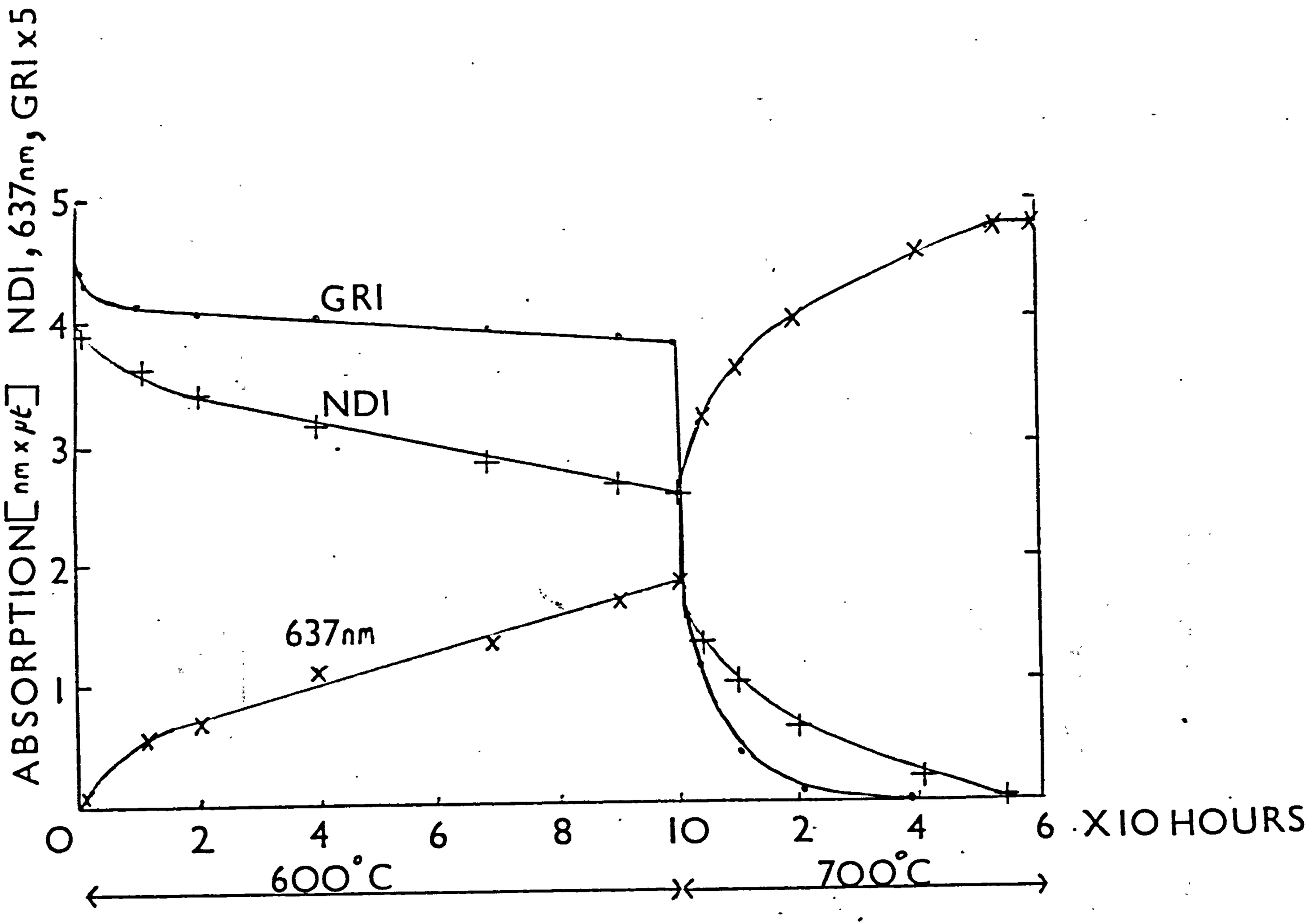



FIG. 5.13

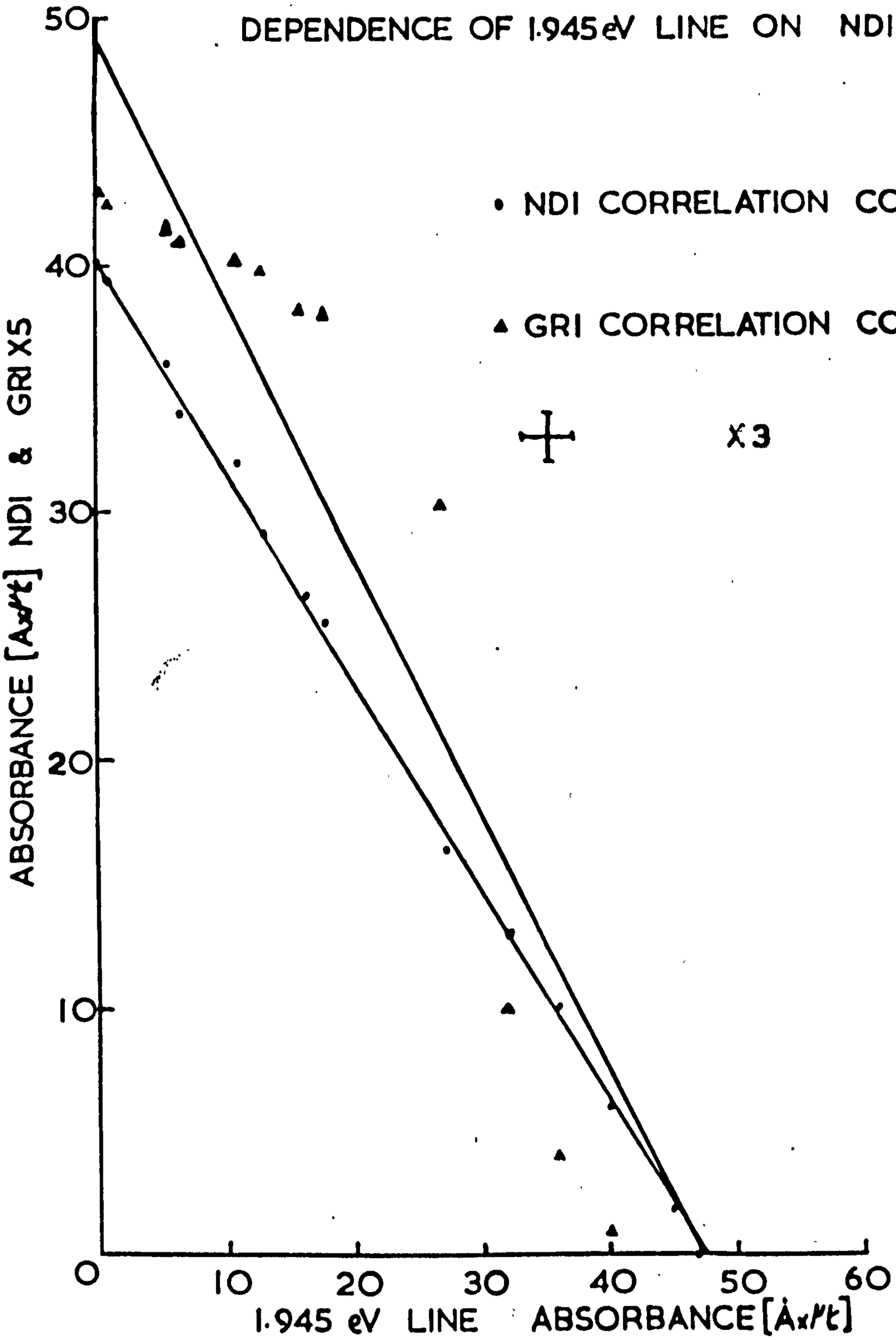

DEPENDENCE OF 1.945 eV LINE ON NDI & GRI
• NDI CORRELATION COEFF. 0.99
▲ GRI CORRELATION COEFF. 0.89
X3
ABSORBANCE [Å×μt] NDI & GRI X5
50
40
30
20
10
0
10
20
30
40
50
60
1.945 eV LINE ABSORBANCE [Å×μt]

FIG. 5.14

In fig. 5.14, the 1.945 eV absorption is shown as a function of both GRI and NDI systems. It is seen that a far better linear relationship exists between the NDI and 1.945 eV systems than between the GRI and 1.945 eV systems. The correlation coefficients of the best linear fits, obtained as described previously are 0.99 and 0.89 respectively, strongly suggesting that the NDI interstitials are trapped by isolated nitrogen atoms to produce 1.945 eV centres.

## Sec. 5.6 Conclusion.

The foregoing analysis has dealt with the role played by the NDI and GRI defects, in type Ia and type Ib diamond, in the formation of new defect centres during thermal annealing of such diamonds. Despite the similarity of annealing rates of GRI and NDI systems, it has been shown that the NDI system consistently correlates more closely with the formation of H3 and H4 systems in type Ia diamond, and also that a relatively simple model unites the results of several such diamonds. Possibilities have been suggested for the infrequent production of the weak H2 absorption system.

A major anomaly at the present time is the nature of any products of annealing which are derived from GRI centres. Palmer (1961) has suggested that the TH5 band is produced by the merging of two GRI vacancies, but the TH5 band is not produced in all diamonds as might be expected on this model. The H2 system is

produced only in some type Ia diamonds and consequently it, also, is unlikely to be associated with GRI centres only.

# Chapter 5

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## Chapter 6

### Conclusion and suggestions for future work.

In this chapter some final conclusions are assembled, along with suggestions for continuation of the measurements presented in this work.

Chapter 3 has been concerned with a survey carried out on a range of synthetic diamonds having impurity nitrogen concentrations of between 10p.p.m and 200p.p.m. The first problem arising from optical studies of such diamonds is that of the occurrence and relative intensities of various infra-red absorption features. The Raman phonon at 165 meV is excited only in diamonds of relatively high impurity nitrogen content, but not in all such diamonds, and there is no relationship between the absorption at 165 meV and that at 140 meV which is known to be nitrogen dependent. Similar anomalies exist concerning absorption at 166.6 meV which is presumably due to a localised vibration centred on nitrogen atoms. Absorption at 165 meV and 166.7 meV is independent of catalysts used in the growth of synthetic diamonds although the chemical nature of such catalysts noticeably affects the details of the nitrogen induced one phonon absorption around 140 meV. It will be of value to ascertain the concentration of dispersed impurities other than nitrogen which are present in such diamonds in order to establish if such impurities could be responsible for suppression of the Raman and 166.7 meV phonons

After radiation damage by 2MeV electrons several hitherto

unreported absorption systems have been observed in synthetic diamonds. Three such systems, having zero phonon lines at 1.883 eV, 1.979 eV, and, 2.367 eV have been found to be dependent for their formation upon isolated nitrogen in the lattice. Since the properties of an interstitial nitrogen atom are reflected in the behaviour of the NDI system these new systems are presumably the result of more complex sitings or charge states of such nitrogen. Stress analysis may prove useful in identification of the nature of the centres involved. In spite of the multiplicity of absorption systems produced by radiation damage in nitrogen containing diamond, no correlations whatever were found between such systems and the various features of the nitrogen induced one phonon absorption, including the Raman and 166.7 meV phonons.

A previously unreported radiation damage zero phonon line has been observed at 2.443 eV which would appear to be independent of nitrogen content. This system was not found to be related to the GRI system and further investigation into this apparently intrinsic defect are required. In addition some absorption systems have been observed to exhibit a spurious occurrence in diamonds of nominally similar impurity content. The nature of other impurity centres than nitrogen will further be of value in the resolution of such problems.

Cathodoluminescence studies have shown the well documented 2.155 eV emission system to be largely independent of

known impurity content. A weak emission system around 795 meV has been seen to be associated with the 2.155 eV system, the latter having also been detected in absorption during this work. Growth of 2.155 eV emission during cathodoluminescence has been seen not to affect the GRI system, produced by a neutral vacancy in the lattice (Clark and Walker 1973), and the nature of this apparently intrinsic defect centre is not understood.

The role played by nitrogen in the production of radiation damage systems in synthetic diamond may be partially resolved by doping such diamonds with the $N^{15}$ isotope, and observing changes in the phonon replicas of zero phonon lines produced by damage centres.

Chapter 4 has reported investigations into some properties of one particular, nitrogen dependent, absorption system observed after radiation damage in natural and synthetic type Ib diamond. The temperature dependence of the system has been analysed in terms of a Debye spectrum of phonons with a cut off energy of 65 meV. The electronic transition at 2.367 eV is seen to couple most strongly with phonons of energy 51 meV, and the Huang-Rhys factor and Debye temperature associated with the transition have been found to be in accordance with those of other such vibronic systems in diamond.

The centre has been observed to take part in a charge transfer process with other optical centres. The 2.367 eV defect is ionised by photons of that energy, charge being returned to the centre by thermal repopulation. The repopulation is highly

temperature dependent, and no mathematical model has been found to fit the process at low temperatures, possibly because many centres accept charge released from 2.367 eV centres. The system readily anneals out at 300°C , without consequent production of another system in the region 2.0 eV to 2.7 eV. Further investigation of the fast optical bleaching at low temperatures,using very low intensity light sources,may prove useful in ascertaining further details of the photo-ionisation of 2.367 eV centres.

Chapter 5 has dealt with annealing of radiation damage centres in type Ia and Ib natural diamond. The results have suggested that the NDI nitrogen interstitial in type Ia diamond is trapped, during annealing, by the A and B nitrogen aggregates, thereby producing the H3 and H4 absorption systems. The results of several type Ia diamonds have been found to be mutually consistent in predicting the relative absorption cross sections of H3 and H4 centres, if one considers the NDI centre to be responsible for their production, and such predictions are in quantitative agreement with those of previous workers, obtained by different means. The uncertainties involved in the measurements of the above quantities will be reduced by carrying out similar analyses on a larger number of specimens of very different A and B nitrogen concentrations.

In agreement with du Preez (1965) the GRI system was found to anneal more quickly, during the early stages of annealing, in those diamonds of highest nitrogen content. This is possibly the result of GRI centres being predominantly close to nitrogen

in the lattice (Davies 1974), thereby enabling GRI centres to combine more readily to produce TH5 centres, on the model of Palmer (1961). The proximity of GRI centres to nitrogen may also explain the saturation of GRI annealing at a given temperature and the continual reduction of GRI linewidth during annealing. Such saturation effects of the NDI system are not, however, accompanied by continual linewidth reduction.

The question of the formation of H2 centres in some type Ia diamonds is still unresolved, but it is possibly related to a third, rare, type of nitrogen aggregate, or the "platelets" in such diamonds. Attempted correlations involving H2 production, along the lines of those carried out in Chap. 5 may prove useful in its identification.

Chapter 5 has also suggested that the 1.945 eV system in type Ib diamond is formed by the migration of NDI centres to isolated nitrogen in the lattice. This conclusion is at variance with that of Hamer and Davies (1976), who, as a result of studying the splitting, in absorption, of the first phonon replica of the 1.945 eV zero phonon line, have concluded that the properties of the system are commensurate with those of a vacancy - nitrogen pair. Such a pair would be produced if the GRI vacancy, not the NDI interstitial nitrogen, migrated to an isolated nitrogen atom during annealing. There is, however, considerable doubt concerning the validity of stress analyses which led to the identification of the GRI centre as a vacancy (Davies 1976), and, consequently, the role of the GRI centre is still in doubt at this time.

# Chapter 6

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| | | |
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## Appendix to Chapter 4

### The 2.367 eV absorption zero phonon line in type 1b diamond

It has been seen that the zero phonon line in question is reduced in intensity when radiation of energy above 2.367 eV is incident on a type 1b diamond which exhibits this system. The fact that the 2.367 eV system is well described by the theory associated with vibronic transitions suggests that the absorption at 2.367 eV represents a transition between the ground and excited states of the appropriate centre. Such a transition would not, of itself, cause bleaching of the system which must hence come about as a result of some other mechanism removing charge from the excited state, to be trapped at other centres in the diamond. The charge transfer from the excited state must proceed at an extremely low rate since bleaching of the 2.367 eV line requires hundreds of minutes even when the radiation from a 100 W lamp is focused onto the specimen. The release of charge from the excited state cannot be a consequence of thermal ionisation of the excited centre since such a process would lead to faster bleaching at higher temperatures, whilst the opposite is found to be the case in practice.

A similar situation exists in diamond when the ND1 zero phonon line is bleached by ultra violet light and the GR1 zero phonon system is enhanced as a consequence. By contrast with the temperature dependence of 2.367 eV bleaching, the broad band of F centre absorption in alkali halides is bleached at a rate which increases with increasing temperature as a result of photon excitation to an excited state being followed by thermal ionisation which releases charge to be trapped elsewhere and produce F′ centres (Markham 1952).

Equation 4.2, page 91, has predicted an exponential behaviour of the bleaching rate of the 2.367 eV system. An equation of this general form describes the experimental situation at high temperatures quite well, but no possible combination of parameters Ci and Ei can describe the bleaching curves at temperatures below about 150K no matter how many different centres are postulated to trap charge released from 2.367 eV centres, since below this temperature the experimental curves deviate markedly from an exponential behaviour of absorption as a function of time. The results of fig. 4.3 are representative of those recorded for a range of diamonds, which consistently showed deviation from exponential behaviour at about 150K. In particular, at low temperature, the system bleached out too rapidly to reliably obtain measurements of absorption coefficients as a function of time. For example, at 5K the line was bleached to extinction after 2 minutes and at 20K it disappeared after 13 minutes.

If one postulates that charge is thermally released from the traps to repopulate the 2.367 eV centres then a measure of the thermal energy required can be obtained by assuming only one centre traps charge released from 2.367 eV centres, although, for reasons discussed above, such a model cannot possibly describe the low temperature situation. Such a postulate results in equation 4.2 taking the form given, where

$$\beta = C \exp^{-E/kt}$$

Analysis of the high temperature bleaching curves yields the parameters

$E \approx 140$ meV , $\frac{\alpha}{C} \approx 10^{-3}$.

Since $\alpha$ depends on the photon flux no value of C can be quoted.

Whilst a thermal activation energy of $\approx$ 140 meV is thus expected for the repopulation of 2.367 eV centres, such repopulation is not brought about by photon energies corresponding to vibronic transitions at centres accepting charge from bleached 2.367 eV centres i.e. energies of 1.9 eV to 2.3 eV.

Similar behaviour is also shown by the charge transfer processes between the ND1 and GR1 centres. A previously enhanced GR1 system is not bleached by photons of energy 1.673 eV but is reduced in intensity by heating the specimen to about 400°C (i.e. a thermal activation energy $\approx$ 55meV), with consequent repopulation of ND1 centres (du Preez 1965).

Again, such behaviour is at variance with the results of shining light of energy in the F′ band onto an alkali halide, as a result of which the F′ band is reduced and the F band enhanced. (However in diamond the ND1 can be repopulated by absorption in the GR1 ultra violet continuum).

It is thus seen that equation 4.2 is far too simple a model to describe the photochromic behaviour of the 2.367 eV centre, or indeed other similar phenomena in diamond and further theoritical investigations into the possible mechanisms of charge transfer between centres would appear to be necessary.

## References


Markham J J (1952) Phys. Rev. 88, 500

du Preez L (1965) Ph.D Thesis Univ. of Witwatersrand